

# **N-O ACTIVATION ON PRECIOUS METAL-FREE METAL OXIDE BASED NO<sub>x</sub> REMOVAL SYSTEMS**

A DISSERTATION SUBMITTED TO  
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE  
OF BILKENT UNIVERSITY  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE DEGREE OF  
DOCTOR OF PHILOSOPHY  
IN  
CHEMISTRY

By  
Kerem Emre Ercan  
January 2022

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January 2022

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

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ABSTRACT

N-O ACTIVATION ON PRECIOUS METAL-FREE  
METAL OXIDE BASED NO<sub>x</sub> REMOVAL SYSTEMS

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January 2022

Elevated operational costs of platinum group metal (PGM) based environmental catalytic systems shift the focus of catalysis research towards cost-effective materials. In search for PGM-free alternative catalytic materials for NO<sub>x</sub> removal, high catalytic performance and long catalyst lifetime emerge as two important technical challenges. Within the scope of this dissertation, novel B-site mixed perovskites LaCo<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub> ( $x = 0.1-0.9$ ) and Fe and/or Co based CeO<sub>2</sub> catalysts were synthesized, investigated and optimized as high performance, PGM-free, and durable catalyst alternatives for NO<sub>x</sub> removal systems. The perovskite based catalytic architectures can be utilized as diesel oxidation catalyst (DOC) oxidizing NO/CO to NO<sub>2</sub>/CO<sub>2</sub>, which can be coupled with selective catalytic reduction (SCR) catalysts to reduce NO<sub>x</sub> species to N<sub>2</sub>. On the other hand, Fe/Co based CeO<sub>2</sub> systems can be exploited as catalyst candidates in SCR of NO<sub>x</sub>. In both of these NO<sub>x</sub> aftertreatment systems, NO activation is required. A simple and reproducible synthetic protocol was utilized to obtain perovskite-based DOC catalysts whose comprehensive structural characterization was carried out via XRD, N<sub>2</sub> adsorption-desorption isotherm, ICP-MS, TEM, H<sub>2</sub>-TPR, *ex-situ* and *in-situ* XANES, EXAFS, *in-situ* FTIR, XPS, and TPD techniques. The oxidative catalytic performance of the perovskites for CO and NO oxidation was determined in flow-mode catalytic activity tests. It was demonstrated that bulk-oxygen vacancies have a strong influence on the redox activity of the B-site mixed perovskites with the ABO<sub>3</sub> structure (where A = La, B = Co, Mn) allowing them to efficiently switch between high and low oxidation states in a reversible fashion under relatively moderate redox conditions without requiring elevated temperatures for regeneration, unlike conventional LaMnO<sub>3</sub> and LaCoO<sub>3</sub>-based simple perovskite systems. La<sub>1.01</sub>Co<sub>0.75</sub>Mn<sub>0.24</sub>O<sub>2.97</sub> and La<sub>1.04</sub>Co<sub>0.65</sub>Mn<sub>0.31</sub>O<sub>2.97</sub> were found to reveal the best NO and CO oxidation performances among the currently investigated perovskites

( $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{2.97}$ ,  $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{2.97}$ ,  $\text{La}_{0.97}\text{Co}_{1.03}\text{O}_{2.91}$ , and  $\text{La}_{0.97}\text{Mn}_{1.03}\text{O}_{3.17}$ ), which were on par with a conventional precious-metal benchmark catalyst (*i.e.*, 1 wt. % Pt/ $\text{Al}_2\text{O}_3$ ). Influence of Fe and Co loading on monometallic (Fe or Co) or bimetallic (Fe-Co) catalysts with different  $\text{CeO}_2$  support materials were studied in SCR of NO to  $\text{N}_2$ . The flow-mode NO reduction experiments point out that 4 wt. % Co/ $\text{CeO}_2$  is the best catalyst in the studied group of catalysts based on its high  $\text{N}_2$  selectivity at relatively low temperatures. Detailed structural characterization experiments conducted via XRD,  $\text{N}_2$  adsorption-desorption isotherm, ATR-FTIR, Raman, and *in-situ* FTIR techniques indicate correlations between catalyst structure and SCR functionality. Our experimental findings indicate that 4 wt. % Co/ $\text{CeO}_2$  has relatively higher catalytic performance under excess  $\text{H}_2(\text{g})$  concentrations. The NO activation performance of both  $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{2.97}$  and  $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{2.97}$  B-site mixed perovskites and 4 wt. % Co/ $\text{CeO}_2$  were tested under significantly harsh conditions indicating their strong potential to be used not only in mobile applications but also in stationary  $\text{NO}_x$  removal systems.

Keywords: Perovskite, Diesel Oxidation Catalyst, Selective Catalytic Reduction, NO activation,  $\text{NO}_x$ , PGM-free, Heterogeneous Catalyst.

# ÖZET

## DEĞERLİ METAL İÇERMEYEN METAL OKSİT TABANLI NO<sub>x</sub> GİDERİM SİSTEMLERİ ÜZERİNDE N-O AKTİVASYONU

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Platin grubu metalleri (PGM) yani değerli metaller içeren, hava kirliliğine yönelik, heterojen katalitik sistemlerin yüksek maliyetlerinden ötürü, kataliz araştırmalarının odağı, ekonomik verimliliği yüksek malzemelere doğru kaymıştır. NO<sub>x</sub> giderim süreçlerinde, yüksek katalitik performans ve uzun kullanım ömrü, alternatif katalitik malzemeler için başlıca hedeflerdir. LaCo<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub> ( $x = 0.1-0.9$ ) yapısındaki özgün B-siteleri karıştırılmış perovskit katalizörler ile Fe ve/veya Co içeren tek metalli (Fe veya Co) veya çift metalli (Fe-Co) CeO<sub>2</sub> destekli katalizörler; bu tez kapsamında, yüksek performanslı, PGM-içermeyen ve dayanıklı NO<sub>x</sub> giderim sistemleri olarak sentezlenmiş, incelenmiş ve optimize edilmiştir. Perovskit tabanlı katalitik yapılar, dizel oksidasyon katalizörü (DOC) olarak NO ve CO'yu, NO<sub>2</sub> ve CO<sub>2</sub>'ye oksitlemek için önerilmektedir. Diğer yandan, Fe/Co tabanlı CeO<sub>2</sub> yapıları ise, seçici katalitik indirgenme (SCR) süreçlerinde, NO<sub>x</sub> giderimi için aday katalizörler olarak incelenmiştir. DOC ve SCR süreçlerinde, sırasıyla, NO'nun oksitlenmesi veya indirgenmesi yoluyla N-O bağ aktivasyonu esastır. Basit ve tekrarlanabilir bir yöntem ile sentezlenen perovskit tabanlı DOC katalizörleri, XRD, N<sub>2</sub> adsorpsiyon-desorpsiyon izoterm, ICP-MS, H<sub>2</sub>-TPR, TEM, *yerinde olmayan (ex-situ)* ve *yerinde (in-situ)* XANES, EXAFS, *yerinde* FTIR, XPS ve TPD yöntemleri ile incelenmiştir. Perovskitlerin NO ve CO oksitleme performansı, akış ortamında gerçekleştirilen katalitik performans testleri ile belirlenmiştir. LaMnO<sub>3</sub> ve LaCoO<sub>3</sub> tabanlı sıradan perovskit sistemlerinin aksine, B-siteleri karıştırılmış perovskitlerin yapısında bulunan külçe (*bulk*) oksijen boşluklarının, perovskitlerin redoks aktivitesi üzerinde önemli bir etkisi olduğu saptanmıştır. Ayrıca, B-siteleri karıştırılmış perovskitler, çok yüksek sıcaklıklar gerektirmeden, tersinir bir şekilde, indirgenme/yükseltgenme (redoks) döngülerini başarıyla tamamlayarak, kendilerini yenileyebildikleri gösterilmiştir. Katalitik NO ve CO oksitleme testlerinde, La<sub>1.01</sub>Co<sub>0.75</sub>Mn<sub>0.24</sub>O<sub>2.97</sub> ve La<sub>1.04</sub>Co<sub>0.65</sub>Mn<sub>0.31</sub>O<sub>2.97</sub> B-

siteleri karıştırılmış perovskitler, incelenen katalizör kümesi ( $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{2.97}$ ,  $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{2.97}$ ,  $\text{La}_{0.97}\text{Co}_{1.03}\text{O}_{2.91}$  ve  $\text{La}_{0.97}\text{Mn}_{1.03}\text{O}_{3.17}$ ) içinde, en iyi performansı göstermiştir. Ayrıca bu katalizörlerin, konvansiyonel PGM referans katalizörü (1 wt. %  $\text{Pt}/\text{Al}_2\text{O}_3$ ) ile benzer oksitleme yeteneğine sahip olduğu ortaya koyulmuştur.

$\text{NO}$ 'nun seçici katalitik olarak  $\text{N}_2$ 'ye indirgenmesi için,  $\text{CeO}_2$  destek malzemesi üzerine, farklı miktarlarda Fe ve/veya Co yüklenmesiyle, tek metalli (Co, Fe) veya çift metalli (Fe-Co) katalizörler elde edilmiş ve metal yükleme miktarlarının katalitik performansa etkisi, farklı katalitik destek malzemeleri üzerinde incelenmiştir. Katalitik  $\text{NO}$  indirgenmesi testlerinde elde edilen bulgular, 4 wt. %  $\text{Co}/\text{CeO}_2$  malzemesinin, incelenen diğer katalizörlere göre, en düşük sıcaklıkta ve en yüksek  $\text{N}_2$  seçiciliğini sağladığını ortaya koymuştur. XRD,  $\text{N}_2$  adsorpsiyon-desorpsiyon izoterm, ATR-FTIR, Raman, XPS ve *yerinde* FTIR teknikleri kullanılarak, katalizör yapısı ve SCR işlevselliği arasındaki ilişkiler incelenmiştir. 4 wt. %  $\text{Co}/\text{CeO}_2$  katalizörünün, incelenen diğer  $\text{CeO}_2$ -destekli katalizörlere göre, yüksek oranda  $\text{H}_2(\text{g})$  içeren şartlarda, yüksek  $\text{NO}$  indirgenme performansı gösterdiği saptanmıştır. İşbu çalışmada kullanılan,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  ve  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  B-siteleri karıştırılmış perovskitlerin ve 4 wt. %  $\text{Co}/\text{CeO}_2$  katalizörünün  $\text{NO}$  aktifleştirme performansları, oldukça zorlu katalitik deney şartları altında test edilmiştir. Bu sebeple, ilgili katalizörlerin hem mobil  $\text{NO}_x$  giderim sistemlerinde hem de durağan  $\text{NO}_x$  giderim sistemlerinde kullanım potansiyeli olduğu öngörülmektedir.

Anahtar Kelimeler: Perovskit, Dizel Oksidasyon Katalizörü, Seçici Katalitik İndirgenme,  $\text{NO}$  Aktivasyonu,  $\text{NO}_x$ , PGM, Heterojen Katalizörler.

## Acknowledgements

First, I would thank to my advisor, Dr. Emrah Özensoy for his unconditional support, help and patience during my Ph.D. studies. Dr. Özensoy's enthusiasm for science motivated me to be a part of his team. His guidance on my scientific journey has played the most influential role in the completion of this dissertation.

In addition to this, I would like to express my thanks to my Ph.D. thesis committee, Dr. Şefik Süzer, Dr. Ömer Dağ, Dr. Nuray Oktar, and Dr. Gökhan Çelik for their precious time.

I also would like to express my deepest gratitude to Merve Kurt for her continuous support and help during my Ph.D. studies. I also would like to extend my sincerest appreciation to my lab colleagues, Abel Tetteh Sika-Nartey, Sinem Şenol, Dr. Zafer Say, Dr. Mustafa Karatok, Dr. Yusuf Koçak, Bartu Karakurt, Gökberk Katırcı, Dr. Muhammed Irfan, Merve Tohumeken, Aybegüm Samast Ok, Dr. Deniz Erdoğan and rest of the Özensoy group members for their valuable scientific discussions, help, and friendship.

I would like to send my special thanks to Aydın Kahrıman as a loyal, knowledgeable, talented and reliable fellow. I also want to acknowledge my friends, Dr. Ahmet Koç, Melik Ö. Özer, Emre Turna, Emre Çağırıcı, Dr. Ahsan Jalal, Ömer Geredeli, Mustafa Akay, and Abdulkadir Dilmen for their strong friendships and valuable time. I also thank to Buğra Eyidoğan for his help in flow reactor drawings. Lastly, I would like to thank to my manager at Roketsan Inc., Dr. Hacı Eşiyok.

Special thanks to Bilkent Chemistry Department faculty, Dr. Burak Ülgüt, Dr. Ferdi Karadaş, Dr. Yunus Emre Türkmen, and Dr. Bilge Baytekin for their valuable time and scientific discussions.

I acknowledge Scientific and Technological Research Council of Turkey (TUBITAK, Grant Number 213M585), Bilkent University Department of Chemistry, Turkish Accelerator And Radiation Laboratory (TARLA) project founded by the Ministry of Development of Turkey (Grant number DPT2006K-120470), Turkish Energy, Nuclear, and Mineral Research Agency (TENMAK), European Cooperation in Science and Technology (COST) action: CHAOS- CA15106 (C-H Activation in Organic Synthesis) and H2020 CalipsoPlus projects for research and travel funding.

Last but not definitely least; I would like to express my deepest and sincerest gratitude to my father Adem Ercan, mother Meryem Ercan, sisters Beyza Nur Ercan, and Melike Nur Ercan for their endless love, support and trust. I also want to thank to my grandfather and grandmother Keramettin Ercan and Hayriye Ercan who passed away. Lastly, I want to thank to my uncle Atila Ercan and my cousin Ahmet Serkan Altınok for their emotional support during my whole education life.

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# CHAPTER 1

## 1. Introduction

### 1.1. Fundamentals of Catalyzed Reactions

In a chemical reaction, formation of a new chemical bond while breaking the other is essential for chemical transformation of reactants to products. While chemical activation of a bond requires energy; bond formation releases energy. The net difference between energy consumption and release for a chemical reaction describes the exothermicity or endothermicity of the reaction. The RR (reaction rate) of a particular reaction depends on the concentration(s) of reactant(s) and rate constant(s). The dependence of the rate constant of an elementary reaction to temperature is defined by the Arrhenius equation, which can be mathematically written as:

$$k = Ae^{-E_a/RT} \quad 1-1$$

where,  $k$  is the rate constant,  $A$  is the pre-exponential factor [1],  $E_a$  is the activation energy,  $R$  is the ideal gas constant, and  $T$  is temperature. The rate constant of a unimolecular reaction can be increased by decreasing  $E_a$ , increasing pre-exponential factor or increasing the temperature. Catalysts are added to chemical reaction systems in an attempt to accelerate the reaction rate by altering the pre-exponential factor and/or activation energy. The appropriate catalyst for a given reaction enables the formation of highly accessible transition states that are entropically and energetically available to reactants. In many cases, a convenient catalyst, chosen for a specific reaction, provides energy efficiency by decreasing the activation energy required for product formation (**Figure 1-1**).

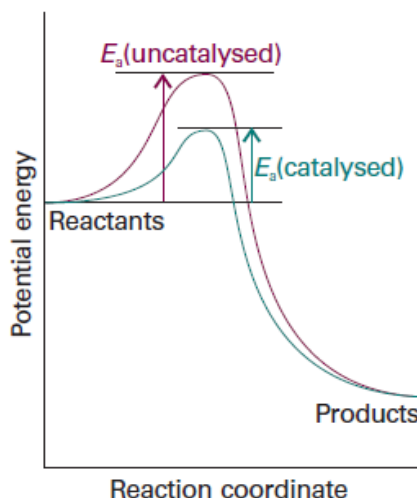


**Figure 1-1.** Activation energy ( $E_a$ ) comparison of catalyzed and uncatalyzed reaction [1]. Copyright (2020) Oxford Publishing Limited.

## 1.2. Catalyst Use in Industrial Chemical Reactions

During the 19<sup>th</sup> and early 20<sup>th</sup> century, majority of industrial reactions were executed via non-catalytic chemical routes at elevated temperatures and pressures to reach sufficient reaction rates [2]. These harsh reaction conditions resulted in material damage in the chemical setup/reactors by corrosion or stress/strain related fatigues and energy costs. Later technological improvements on catalyst use in industrial chemical processes led to the achievement of two significant milestones [2]:

- Higher reaction rate at relatively lower pressures and temperatures
- The reactant and catalyst contact enhancement (catalyst bed engineering) for continuous flow conditions improved operational efficiency of reactant transformation to products

Some of the industrially and environmentally significant reactions and their catalysts were presented in **Table 1-1**. Hence, the economic/environmental significance of these reactions (as well as others not given here) have greatly increased the interest in the use of catalysts in industrial processes and have been an important source of inspiration for scientific studies to enlighten the fundamentals of corresponding catalytic processes.

**Table 1-1.** The Development of Important Industrial Catalytic Processes [2]. Copyright (2020) Wiley.

| Year of First Commercialization | Process/Reaction                                                                                                                 | Catalyst                                                         | Area of Industry                       |
|---------------------------------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------|
| 1875                            | Sulfuric acid manufacturing<br>$\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$                                             | Pt, $\text{V}_2\text{O}_5$                                       | Chemicals                              |
| 1903                            | Nitric acid manufacturing<br>$2\text{NH}_3 + 5/2\text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$                         | Pt gauze                                                         | Chemicals                              |
| 1913                            | Ammonia synthesis<br>$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$                                                         | Fe/ $\text{Al}_2\text{O}_3$ / $\text{K}_2\text{O}$               | Chemicals<br>Fertilizers               |
| 1923                            | Methanol synthesis<br>$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$                                                 | CuZnO                                                            | Chemicals                              |
| 1930                            | Fischer-Tropsch Synthesis<br>$2\text{CO} + 2\text{H}_2 \rightarrow \text{C}_1\text{-C}_{30} \text{ HCs}$                         | Fe/K/CuO,<br>Co/Kieselguhr                                       | Petroleum                              |
| 1920-40                         | Hydrogenation reactions<br>Hydrogenation of food oils                                                                            | Ni/Kieselguhr, Raney                                             | Petrochemicals<br>Foods                |
| 1976, 1981                      | Auto Emission Control<br>CO and HC oxidations<br>NO Reduction                                                                    | Pt, Pd/ $\text{Al}_2\text{O}_3$ ,<br>Rh/ $\text{Al}_2\text{O}_3$ | Automotive<br>Environmental<br>Control |
| 1980-95                         | Selective catalytic reduction of<br>NO<br>$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ | Pt, Pd/ $\text{Al}_2\text{O}_3$ ,<br>Rh/ $\text{Al}_2\text{O}_3$ | Environmental<br>Control               |

### 1.3. Environmental Catalysis

Despite the advances in green and renewable energy sources, a significant portion of energy production is still obtained by combustion processes of fossil fuels (see **Figure 1-2**). Combustion of fossil fuels lead to air pollution and global warming and thus pose a significant environmental threat. Hence, the environmental catalysis has been developed to reduce the emission of toxic gases in fossil fuel combustion processes, before such contaminants are released to the atmosphere. Some of the major toxic gases generated in industrial and anthropogenic activities include  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ ),  $\text{SO}_x$  ( $\text{SO}_2$  and  $\text{SO}_3$ ), CO, hydrocarbons (HC) and particulate matter (PM) (**Figure 1-3**).

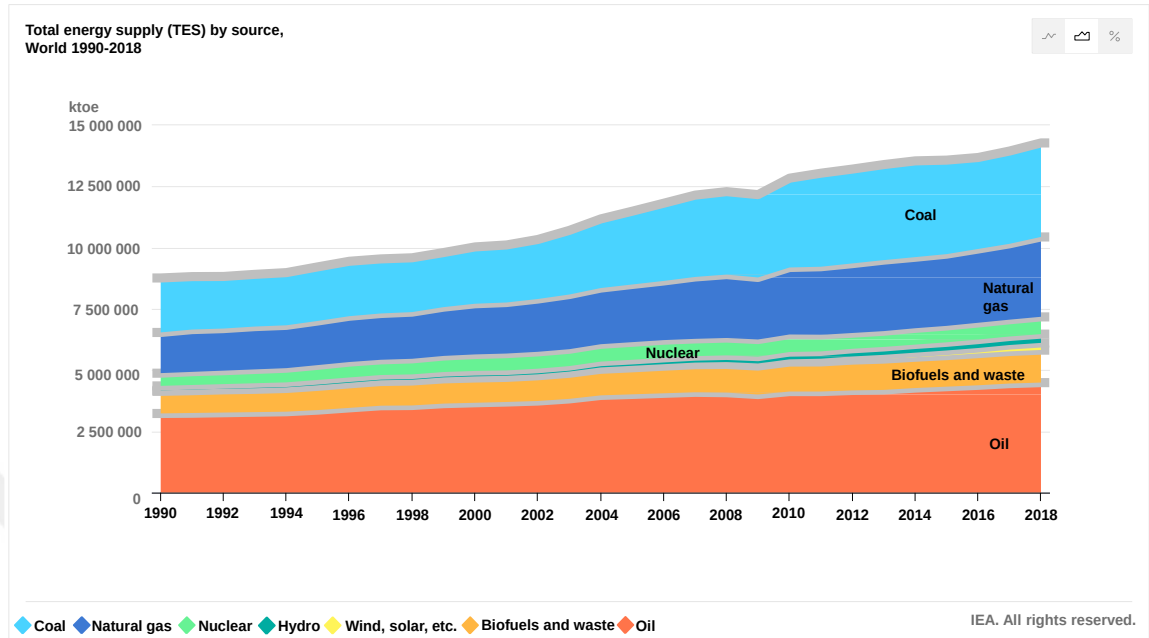


**Figure 1-2.** The energy supply distribution by their sources [3].

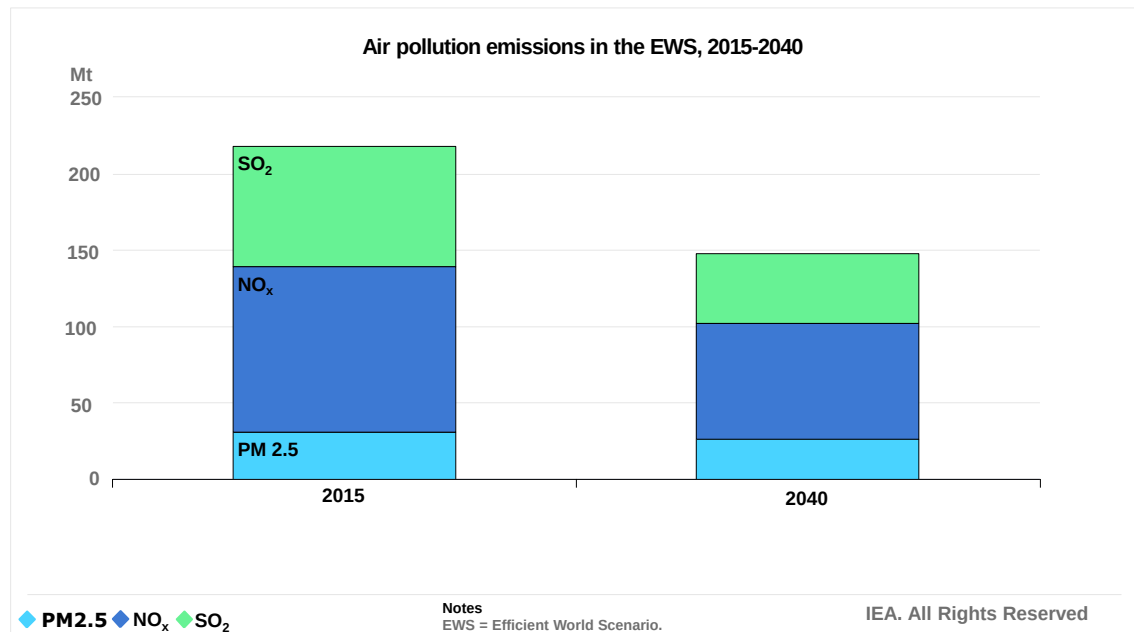


**Figure 1-3.** Contribution of the PM (Particulate matters), NO<sub>x</sub>, and SO<sub>2</sub> to air pollution (2015 and 2040 is expected values depend on the efficient world scenario (EWS) that determined by energy efficiency target of United Nations (UN) Sustainable Development Goal 7 [4]).

### 1.3.1. Emission Control Catalysis for Mobile Sources

Most of the currently used transportation technologies rely on the combustion of diesel, gasoline, liquefied petroleum gas (LPG, a mixture of propane and butane) and kerosene in

engine that results in emissions of NO<sub>x</sub>, SO<sub>x</sub>, HC, CO, and PM emissions. Particularly, NO<sub>x</sub> emissions originating from mobile resources (see **Figure 1-4**) is one of the major contributors to air pollution.

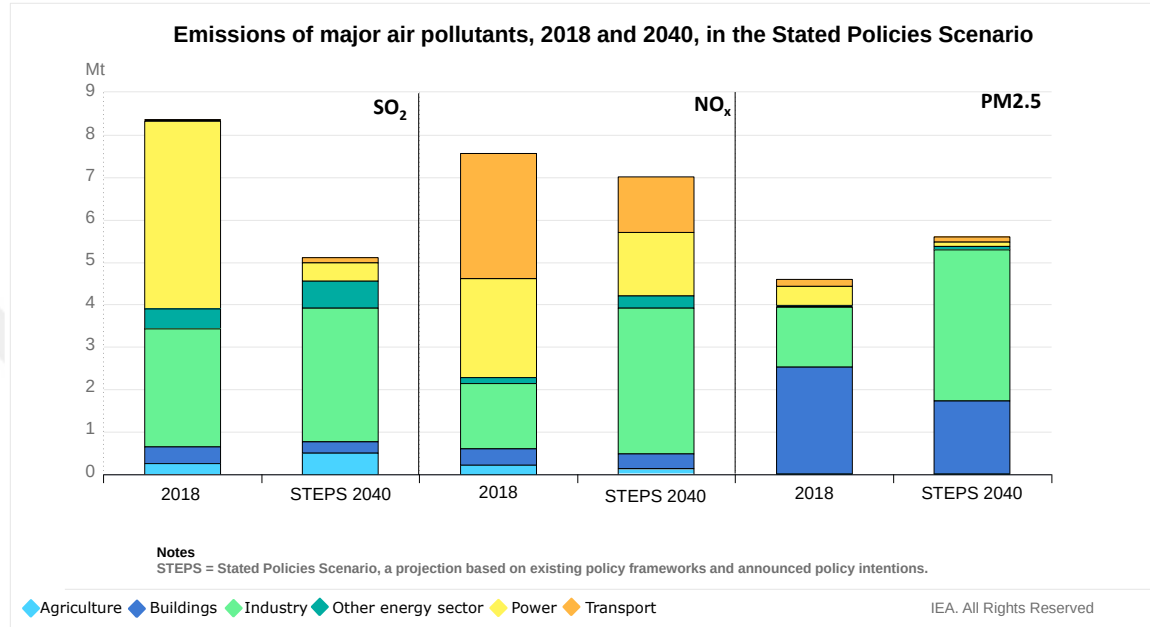


**Figure 1-4.** The distribution of major air pollutants by their sector [5].

In the beginning of 1970's, Clean Air Act law was enforced in U. S. to decrease emissions of NO<sub>x</sub>, CO and HC by 90 % from mobile sources. Hence, automobile industry focused on emission control catalysis to meet the stringent regulations. Emission control catalysis for mobile applications should be typically functioning in the presence of 10 % H<sub>2</sub>O, 10 to 60 ppm SO<sub>2</sub> and various amounts of additional catalytic poisons such as Zn and P, where operational temperature and space velocities are expected to be within 623-1273 K, and 10,000 to 100,000 h<sup>-1</sup>, respectively for an effective catalyst lifetime of 50,000 miles [2]. Therefore, based on the engine type and operational (air to fuel ratio) conditions, different families of catalytic emission control systems have been developed since 1970's.

### 1.3.1.1. Conventional Gasoline Engines

#### 1.3.1.1.1. Three-Way Catalysts (TWCs)

The conventional gasoline engines operate close to the stoichiometric air to fuel ratio, where Three Way Catalyst (TWC) technology is typically used to abate NO<sub>x</sub>, CO and HC in the exhaust [6]–[8].

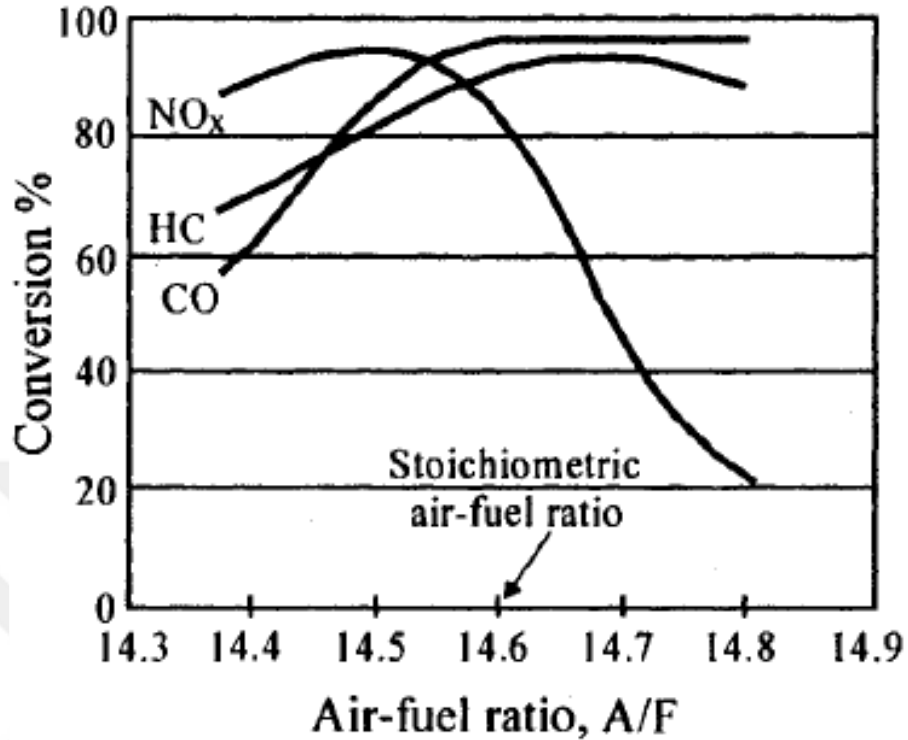


**Figure 1-5.** The catalytic conversion regimes of three primary air pollutants ( $\text{NO}_x$ , CO, and HC) in TWC systems as a function of air to fuel ratio [2]. Copyright (2020) Wiley.

Conventionally, TWC contain Pt, Pd, and Rh active metal sites supported on high-surface area metal oxides, which carry out selective  $\text{NO}_x$  reduction as well as CO and HC oxidation simultaneously. In TWC systems, unburned HC and CO act as reducing agents for  $\text{NO}_x$  reduction while CO and unburned HCs are oxidized with  $\text{NO}_x$  and oxygen in the air. Thus, the weight-based Air to Fuel ratio (A/F) should be optimized for efficient operation of TWC. As can be seen in the conversion regimes given in **Figure 1-5**, while  $\text{NO}_x$  reduction is maximized for A/F within 14.5-14.6 (*i.e.*, rich conditions or low level of air intake for combustion), CO and HC oxidation are maximized at A/F > 14.6. A/F > 14.6 leads to a drastic decrease in  $\text{NO}_x$  reduction and TWC becomes inefficient in the presence of excess air (*i.e.*, lean-burn conditions).

### 1.3.1.2. Lean-Burn Engines

As mentioned earlier, TWC systems are not typically effective in reducing  $\text{NO}_x$  in the presence of excess oxygen (*i.e.*, under lean-burn conditions). However lean-burn engines are more attractive due to their enhanced fuel efficiency (20-30 %) and lesser  $\text{CO}_2$  emissions as compared to classical internal combustion engines [2], [8]–[11]. Lean-burn

engines with an A/F ratio of 20-65:1 (diesel and gasoline) enable low combustion temperatures resulting in smaller NO<sub>x</sub> emissions, higher fuel efficiency (*i.e.*, lesser amounts of unburned HC), and lower CO<sub>2</sub> emissions as compared to classical internal combustion engines. Thus, to maintain efficient NO<sub>x</sub> reduction in the presence of excess oxygen, multiple alternative catalytic approaches have been developed such as selective catalytic reduction (SCR), NO<sub>x</sub> storage and reduction (NSR), and direct NO<sub>x</sub> decomposition catalysts.

### 1.3.1.2.1. NO<sub>x</sub> Storage and Reduction Catalysts (NSR)

The NSR technology has been developed by Toyota Motor Company [12], [13] to provide efficient NO<sub>x</sub> reduction under lean-burn conditions. In the operational cycle of the NSR catalyst, first, the emitted NO<sub>x</sub> species are adsorbed on the NSR catalyst under lean (oxidizing) conditions. Then, these adsorbed (stored) NO<sub>x</sub> species are reduced by an external reducing agent (typically diesel/gasoline fuel) that is injected under rich (reducing) conditions. In other words, NSR catalysts operate in a cyclic fashion where the operational conditions are switched between lean and rich environments in an alternating fashion. Although NSR based catalytic systems are highly efficient, they mostly suffer from sintering of precious group metals (PGM) and PGM deactivation by SO<sub>x</sub> poisoning. Conventional NSR catalysts contain Pt/BaO/Al<sub>2</sub>O<sub>3</sub> structures, where Pt carries out NO and NO<sub>2</sub> oxidation to nitrate/nitrite (see **Scheme 1-1**) which are stored on BaO (*i.e.* the storage domain), while high-surface area porous Al<sub>2</sub>O<sub>3</sub> support provides efficient dispersion of Pt and BaO sites [14], [15].



**Scheme 1-1.** Representative scheme for NO<sub>x</sub> removal on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> [16]. Copyright (2020) Elsevier.

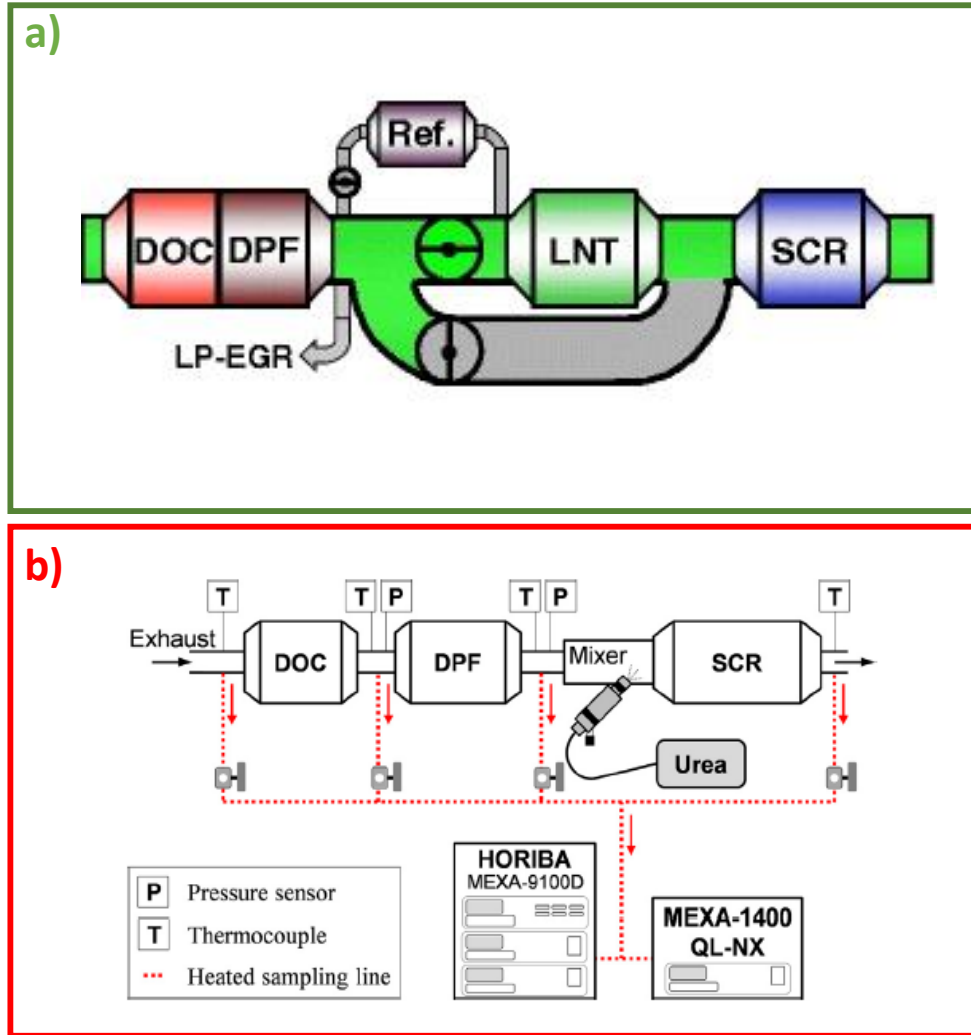
There are numerous attempts to increase sulfur tolerance and NO<sub>x</sub> storage capacity of NSR systems [17]–[21] by modifying catalyst support with different oxides such as ceria, zirconia, and titania. Yet, high cost of PGM and the need for high temperature SO<sub>x</sub> regeneration (> 973 K, leading to extra energy consumption and catalyst aging) continue to be important technical limitations of NSR based DeNO<sub>x</sub> systems.

#### **1.3.1.2.2. Direct NO<sub>x</sub> Decomposition**

Direct NO<sub>x</sub> decomposition catalysts are aimed to decompose NO(g) in the exhaust gas stream to N<sub>2</sub> and O<sub>2</sub>. Cu-ZSM-5 is accepted as one of the promising catalysts for direct NO<sub>x</sub> decomposition [22]. The direct NO decomposition does not need an external reducing agent. However, high activation energy, low thermal durability and limited NO<sub>x</sub> decomposition performance [23]–[25] make the application of this technology unfavorable.

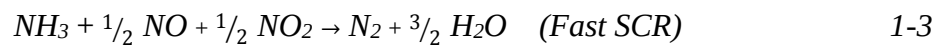
#### **1.3.1.2.3. Selective Catalytic Reduction (SCR) Based NO<sub>x</sub> Removal Systems and Their Components for Diesel Engine Operations**

Aftertreatment technologies mentioned above are mostly convenient for low-sulfur content gasoline and lean burn engines. Since the diesel fuels contain relatively higher levels of sulfur compounds [26], [27] as compared to gasoline, SCR-based catalytic systems along with diesel oxidation catalysts (DOC), diesel particulate filters (DPF), and NSR catalysts have been used simultaneously in lean-burn diesel engine systems. In order to abide stringent emission regulations, highly complex catalytic aftertreatment systems were designed including DOC + DPF + SCR or DOC/NSR + DPF + SCR combinations. Particularly, NSR containing diesel catalytic aftertreatment systems are receiving attention in light-duty vehicles enabling low-temperature NO<sub>x</sub> abatement [28].



**Scheme 1-2.** The typical tailpipe exhaust emission control system configurations for: a) DOC + DPF + NSR (LNT) + SCR and b) DOC + DPF + SCR adapted from Ref [29] and [30] copyright (2020) Elsevier.

The DOC, NSR, and DPF are necessary to increase NO<sub>x</sub> removal efficiency. On the other hand, improvement of the SCR systems with these additional components brings further complexity and limitations. Some of the most prominent reactions in SCR based systems can be listed as follows: Such as



Reaction (1-2) is accepted as the standard SCR reaction where NO concentration is in excess. The reaction (1-3), known as the “Fast SCR” reaction has a higher reaction rate (at

50-60 %  $\text{NO}_2/\text{NO}_x$  stoichiometry) as compared to reactions (1-2) and (1-4). Additionally, when the  $\text{NO}_2$  concentration increases in the gas stream, reaction (1-4) becomes effective [30]. Based on the reactions given above, roles of NSR, DOC and DPF components in SCR-based aftertreatment systems can be explained in more depth.

**Various considerations associated with the presence of an NSR component in SCR systems:**

- $\text{NO}_x$  species are adsorbed and stored on the NSR component as nitrites or nitrates during the lean cycle and they are further reduced (rich cycle) with the injection of a reducing agent (HC and CO [29], [31]).
- Fuel consumption increases due to additional HC used as a reducing agent.
- During the rich cycle, adsorbed  $\text{NO}_x$  is reduced to form onboard  $\text{NH}_3$  which in turn, can be used as an additional reducing agent by the SCR catalyst.
- Need for external  $\text{NH}_3$  injection can be eliminated.
- Due to the  $\text{NO}_2$  storage on NSR component, fast SCR is not feasible.
- Since SCR component is located downstream (after the NSR component) as a secondary De $\text{NO}_x$  catalyst, low  $\text{NO}_x$  abatement activity is observed due to the limited ammonia formation from the NSR catalyst.
- NSR+SCR systems have broad temperature range for  $\text{NO}_x$  reduction.
- Low sulfur tolerance due to Ba, K domains in the NSR component [32].
- NSR+SCR systems are typically preferable for small vehicles [31].

**SCR systems without NSR:**

- SCR component is placed after DOC and DPF.
- Operated continuously under lean conditions.
- Due to  $\text{NO}_2$  formation by the DOC, fast SCR is applicable for  $\text{NO}_x$  removal.
- No fuel penalty.
- External  $\text{NH}_3$  supply is needed (see **Scheme 1-2b**, urea tank).
- $\text{N}_2\text{O}$  formation (a global warming threat [33]) during the  $\text{NO}_x$  reduction by the SCR catalyst, is a primary concern.

- Excess  $\text{NH}_3$  is injected to the gas stream to increase  $\text{NO}_x$  removal efficiency. In order to remove unreacted ammonia, ammonia slip catalysts are added to the downstream of the SCR catalysts [31].
- Useful for heavy-duty vehicles.
- Low activity at low temperatures.

Based on the statements given above, it is extremely important to identify operational needs (*e.g.*,  $\text{NO}_x$  concentration, temperature window for aftertreatment, space availability for urea injection system *etc.*) to determine the most relevant aftertreatment configuration for a selected application.

#### **1.3.1.2.3.1. DOC Components in Aftertreatment Systems**

A typical catalytic tailpipe exhaust-emission control system for diesel engines contains a DOC component to oxidize unburned HC, NO, and CO where SCR is mounted after DOC to reduce  $\text{NO}_x$  species to  $\text{N}_2$  under lean-burn conditions. There are two significant goals of using DOC catalysts which are achieving NO oxidation to  $\text{NO}_2$  for fast SCR (see reaction (1-2)) and heat generation from the exothermic oxidation of NO, HC, and CO to regenerate the DPF component [31]. DOC catalysts may typically contain PGM active sites. Henry *et al.* [34] indicated that the NO to  $\text{NO}_2$  oxidation activity of Pt/Pd based DOC catalysts was suppressed in the presence of HC in gas stream.  $\text{NO}_2$  formation is inhibited due to competition between NO and long chain alkenes for surface oxygen atoms. In addition, the stability of PGMs on the DOC catalyst is another serious problem that needs to be tackled. Jen *et al.* [35] investigated the mobility of Pt at elevated temperatures. They verified that Pt in DOC can migrate from DOC to the downstream of the catalytic tailpipe system. Moreover, SCR De $\text{NO}_x$  efficiency may further diminish when the temperature exceeds 1023 K (such high temperatures may be required for DPF regeneration) which leads to  $\text{NH}_3$  loss due to  $\text{NH}_3$  oxidation in SCR by the migrated Pt atoms. Replacement of Pt with Pd for DOC catalyst was suggested to decrease Pt vaporization and downstream Pt migration [36]. Furthermore, Kim *et al.* found out that Pd addition to Pt decreased HC and CO light off temperatures in DOC [37]. Because of high material costs of PGM containing DOC, associated research focus shifts to PGM-free technologies. In this regard, PGM-free perovskite-based DOC systems has become one of the most promising alternatives [32].

### **1.3.1.2.3.2. SCR Components in Aftertreatment Systems**

The main role of SCR catalyst is to selectively reduce  $\text{NO}_x$  species to  $\text{N}_2$  by using  $\text{NH}_3$  as a reducing agent. Cu, Fe-based zeolites and vanadia-tungsten oxide or vanadia-titania-based catalyst families have been developed and commercialized for SCR systems. The Cu zeolite-based SCR catalysts have exceptional activity at low temperatures. However, the limited S tolerance of these catalysts requires high-temperature regeneration at  $T > 773 \text{ K}$  [38]. Fe zeolite-based systems requires high temperature to increase  $\text{NO}_x$  reduction efficiency, while  $\text{NO}_2$  production is needed to enhance low temperature  $\text{NO}_x$  removal efficiency [31]. Vanadia catalysts are relatively low-cost systems but suffer from insufficient stability at high temperatures (at  $T > 823 \text{ K}$ ). Hence, vanadia is not preferred for DPF-integrated SCR systems requiring operational temperatures ( $> 923 \text{ K}$ ) for DPF regeneration. Similar to Fe-zeolite, vanadia based catalysts also need  $\text{NO}_2$  formation for low temperature operation [31]. However, incorporation of Fe and Cu on zeolite enhances low temperature De $\text{NO}_x$  performance as compared to monometallic copper zeolites. Addition of La on Fe-Cu mixed zeolites lead to further lowering of  $\text{NO}_x$  reduction temperature. Another drawback of Fe and/or Cu based zeolites is HC poisoning. The high temperature regeneration of SCR catalysts to remove stored HCs results in thermal aging. Fe-zeolite based SCR catalysts are more susceptible to HC poisoning in comparison to Cu based catalysts [39]. Another crucial problem is the  $\text{N}_2\text{O}$  generation as a result of ammonium nitrate decomposition. If the gas stream has excess  $\text{NO}_2$  (*e.g.*,  $> 50 \%$  of total  $\text{NO}_x$ ), ammonium nitrate formation can occur [31] whose decomposition releases large amounts of  $\text{N}_2\text{O}$ . Kamasamudram *et al.* [40] showed that increased copper loading and more effective DOC design to control the  $\text{NO}_2$  levels can hinder  $\text{N}_2\text{O}$  formation.

### **1.4. Motivation of the Current Study**

In this study, perovskite-based DOC catalysts and Fe and/or Co on  $\text{CeO}_2$  based SCR catalysts were studied to obtain alternative catalytic materials, which are effective in CO/NO oxidation and  $\text{NO}_x$  reduction with enhanced structural stability and improved cost efficiency.

### 1.4.1. PGM-free Perovskites as Oxidation Catalysts

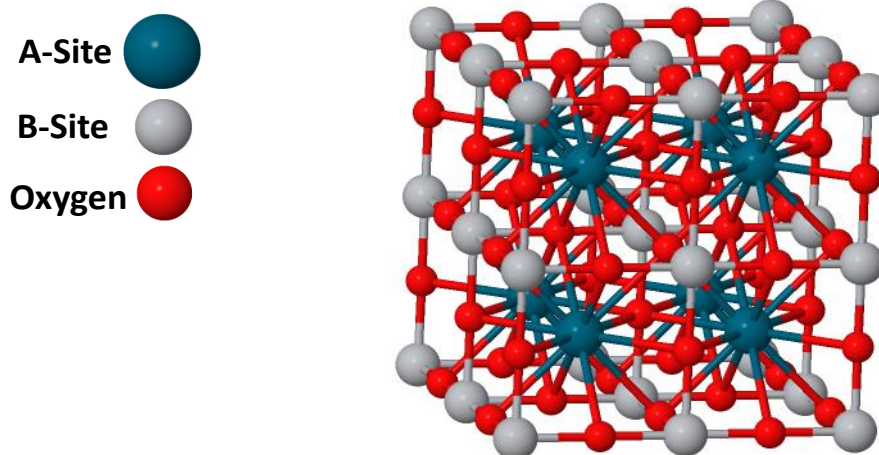
Due to their high costs and dynamic raw material prices, PGM (*e.g.*, Pt, Pd, Ir, Rh *etc.*) containing catalytic systems are typically expensive [41]. An alternative to decrease the cost of these SCR catalytic system is to design PGM-free oxidation catalysts which has been proven to be a challenging task [42]–[45]. Pt-free perovskite-based catalytic systems are potential candidates for novel NO<sub>x</sub> removal technologies due to their decent NO oxidation and NO<sub>x</sub> adsorption capabilities.

Perovskites is a family of metal oxides with a general form of ABO<sub>3</sub> (see **Scheme 1-3**), where A and B are cations and O stands for an oxide anion. Heterogeneous catalytic properties of the perovskites were studied since 1970s [46]–[49]. The main advantage of the perovskite-based heterogeneous catalytic systems is their high activities despite their PGM-free (platinum group metals) nature. In the perovskite-based systems, A site typically constitutes of an alkali, alkaline earth, transition metal or lanthanide cation, where B-site cations are commonly transition metal cations. In conventional LnBO<sub>3</sub> (Ln=Lanthanides) perovskites, both A and B site cations have +3 valence state [50]. In some perovskite systems A and B sites can be doped by external cations to yield A<sub>x</sub>A'<sub>1-x</sub>B<sub>y</sub>B'<sub>1-y</sub>O<sub>3±α</sub> [51]. The external cation doping to A and/or B site leads to distortion of the cubic perovskite structure (see **Scheme 1-3**) resulting in either orthorhombic or rhombohedral crystal structure. The tolerance factor (*t*) can be used to predict the crystal structure stability where durable perovskite crystal structure has “*t*” values within 0.8-1.0 [52]. Moreover, the ideal cubic perovskite has a *t* value that is equal to 1 where the deviation from the ideal perovskite depends on the ionic radii of A and B site cations and substitution degree (fraction) of doped cations.

$$t = (r_a + r_o) / 2^{1/2} (r_b + r_o) \quad 1-5$$

Here, *r<sub>a</sub>*, *r<sub>b</sub>*, and *r<sub>o</sub>* radii of A-site, B-site cations, and O anion, respectively.

### Cubic Perovskite Structure ( $ABO_3$ )



**Scheme 1-3.** Representation of the crystal lattice belonging to  $ABO_3$  unit cell of the cubic perovskite structure (A and B represent different cations).

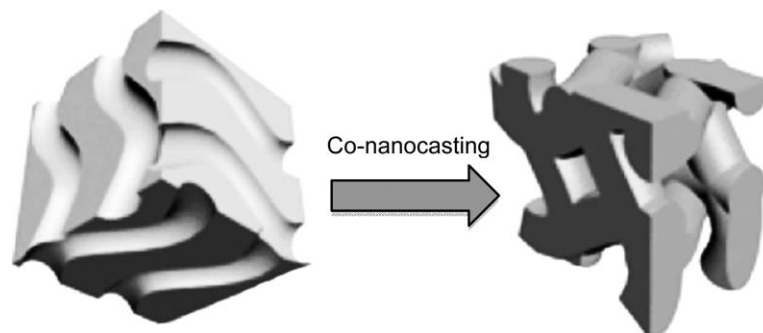
Perovskites have unique redox and charge transfer/mobility properties enhancing their catalytic capabilities [52]–[54]. Superior catalytic activity of perovskites is frequently attributed to their variable oxygen vacancy concentration, defective or non-stoichiometric chemical structure, dynamic surface composition/morphology, and significant redox activity of the B-site cations [55]–[57]. Tuning of the chemical environment around A and B-site cations is crucial for controlling the catalytic activity, thermal stability and defect structure of perovskites [58]. Redox chemistry of perovskites can also be manipulated by doping external cations at A and/or B-sites to form complex structures such as  $A_xA'_{1-x}B_yB'_{1-y}O_{3\pm\alpha}$  [51]. For instance, La-based simple  $LaMnO_3$  and  $LaCoO_3$  perovskites and their A and/or B site substituted complex derivatives have drawn significant attention due to their tunable catalytic properties [59]–[62].

#### Synthesis Methods for Perovskite Structures:

The various methods have been tried for perovskite synthesis to reach enhanced surface area that yields relatively higher catalytic activity. The solid-solid diffusion (ceramic method) synthesis of perovskites proposes solid state mixing of different oxide powders upon thermal activation of oxides. This method is not only relatively slow but also requires high temperatures (*i.e.*, 1273 K) leading to particle sintering (10 to 100 micron) and decrease in specific surface area (1 to 2  $m^2/g$ ) [63], [64]. Solution-mediated perovskite

synthesis, spray/freeze drying, sol-gel, co-precipitation, and complexation of perovskites, have been utilized since 1980s. The fundamental principle of those methods are dissolving precursors in a liquid form solvent that is followed by a successive drying and calcination steps [50], [65]. By using those methods, specific surface area of the perovskites can be increased up to 20 m<sup>2</sup>/g that is almost 10 times higher than the surface area values obtained by the ceramic method. As compared to conventional synthesis of La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub>, relatively high surface area perovskites can be synthesized by citrate method. In this method, all precursors are dissolved in citric acid followed by gel formation and calcination. It was seen that La and Mn cations were replaced with hydrogen atom in –COOH groups by forming complex gel media prior to calcination [66]. La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> perovskites synthesized with citrate method yielded 18.8 m<sup>2</sup>/g surface area after 4 h calcination at 973 K. However, at this synthesis conditions, some of SrCO<sub>3</sub> species were detected by X-ray diffraction (XRD) due to the high carbon content of the gel during calcination [66].

To offer high surface area perovskites, meso-structuring synthesis route was used which also allowed controlling of the porosity of solids. The hard template or nanocasting synthesis routes were utilized for mesostructured perovskite formation. Wang et al. used mesoporous silica as a hard template for mesoporous perovskite synthesis [67]. In this method, porous silica templates were prepared, and metal precursor solution was transferred over the silica template. The precursor embedded silica templates were mixed with citric acid solution. Upon calcination of the dried materials, silica templates were removed with alkaline solution resulting in porous perovskite structure.



**Scheme 1-4.** Silica hard template assisted mesoporous perovskite synthesis (nano-casting); non-etched silica (left), etched (right, LaFe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub>) [68].

Based on mesostructured synthesis routes, high surface area perovskites can be synthesized *i.e.*, 270 m<sup>2</sup>/g [68], [69]. However, high temperature silica abstraction or catalytic oxidation reactions (methane/methanol oxidation) might diminish surface area of the catalyst to 96-69 m<sup>2</sup> or 155-128 m<sup>2</sup>/g (methanol oxidation) [70].

### **Redox Properties of Perovskites:**

The catalytic activity of perovskites is closely related to the reversible redox properties of their B-site cations [71], [72]. It was demonstrated that LaCoO<sub>3</sub> has two distinct reduction temperatures at 673 K and 850 K, where Co<sub>3</sub>O<sub>4</sub> has only reduction at around 600 K [73]. The low temperature reduction of LaCoO<sub>3</sub> can be associated with oxygen deficient perovskite formation, where high temperature reduction results in metallic Co formation. These findings point out that B-site cations in the structure of perovskite are more durable as compared to monometallic oxides. Moreover, the Sr substitution decreases the reduction temperature for La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3-x</sub> to 473 K. The reduction temperature shift of La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> type perovskites [74] can be associated with the reduction of metastable Co<sup>4+</sup>, which was formed by Sr loading together with oxygen vacancy creation. LaMnO<sub>3</sub> also has two reduction temperatures. The first reduction was observed around 673 K and the second one was obtained within 830-1200 K [75]. At temperatures higher than 1200 K perovskite structure is destroyed [76].

### **Oxygen Vacancies in Perovskites:**

Oxygen vacancy formation in perovskites can be controlled by doping external cations at the B-site positions. The external doping of B-site cations can be effective for shifting the following equilibrium  $B^{4+}-(O^{2-})-B^{4+} = B^{3+}-(\square)-B^{3+} + 1/2O_2$  (where “□” stands for oxygen vacancy) [58] in the favor of vacancy formation and higher oxidation state. Molecular oxygen adsorbed on the perovskites can be activated by electron transfer processes at the vacancy sites yielding catalytically reactive oxygen species.

Oxygen Temperature Programmed Desorption (O<sub>2</sub>-TPD) is one of the effective methods to find out the amount of reactive oxygen species that can be generated in perovskites. The desorption temperature of oxygen species through an oxygen vacancy assisted pathway was observed within 573 to 973 K [58]. The low temperature O<sub>2</sub> desorption is denoted as

$\alpha$ -oxygen (originating from reactive  $O_2^-$  and/or  $O^-$  species) and the high temperature oxygen desorption species are denoted as  $\beta$ -oxygen (lattice oxygen) [77], [78].

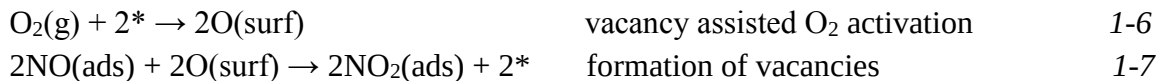
Oxygen mobility characteristics and the concentration of surface defects (i.e., oxygen vacancies) are also essential for the catalytic activity of perovskites. The oxygen diffusion in the perovskite structure can be explained by a hopping mechanism that consists of vacancy diffusion in the lattice [52]. Although there is no experimental method for a conclusive verification of this hopping mechanism, computational potential energy surface maps were used to calculate the energy of defect migration [79]. Based on these calculations, it was shown that oxygen ion vacancies migrated by following the lowest energy path. The computational energy of activated energy for vacancy migration was found to be 0.86 eV which was compatible to other former results (0.76 eV-0.55) [80]. The interstitial mobility of the ions in the perovskite structure requires more energy i.e., 1.5 eV, thus ion mobility in perovskite structure most likely occurs via transportation of oxygen ion vacancies. The ease of vacancy transport improves the reversible redox functionality of perovskites via transportation of vacancies from the bulk to the surface or vice versa.

#### **CO/NO Oxidation on Perovskites:**

In 2002, Nishihata *et al.* [81] reported a so-called “intelligent” Pd-perovskite ( $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ ) catalyst with a relatively higher stability and activity than conventional Pd/ $Al_2O_3$  in CO(g) oxidation and  $NO_x$  reduction reactions. Recently, Kim *et al.* [32] showed that Sr incorporated  $La_{1-x}Sr_xCoO_3$  type perovskites revealed higher NO to  $NO_2$  conversion as compared to the conventional Pt- $Al_2O_3$  catalyst. However, this latter perovskite catalyst had relatively low thermal stability that resulted in catalytic activity loss as a function of ageing of the catalyst. Thermal stability was found to be improved when Co sites were replaced with Mn to obtain  $La_{1-x}Sr_xMnO_3$ . However,  $La_{1-x}Sr_xMnO_3$  revealed lower NO to  $NO_2$  conversion as compared to its Co-based counterpart [32].

Additionally, Kim *et al.* specified that [32] although perovskites show reasonable NO oxidation activity, their CO/HC oxidation capability was limited in the absence of Pd addition. The molecular level of understanding of catalytic oxidation mechanisms over perovskite catalysts is extremely important to design novel and improved catalysts. NO

oxidation on perovskites is commonly explained by the vacancy-mediated Mars-van Krevelen-type mechanisms. In such a catalytic route, initially NO adsorbs on the perovskite surface and then reacts with surface oxygen species leading to the formation of an oxygen vacancy. Generated oxygen vacancy functions as an activation site for molecular oxygen. These steps can be summarized as:



Thus, catalytic activity of perovskites are closely linked to the generation and healing (*i.e.* disappearance or filling) of surface oxygen vacancies [44], [52], [54], [82], [83]. Moreover, Voorhoeve *et al.* [63], [84] showed that CO oxidation reaction follows suprafacial and intrafacial reaction mechanisms represented by Langmuir-Hinshelwood and Mars-Van Krevelen mechanisms, respectively. Hence, the suprafacial mechanism occurs at relatively low temperatures for CO oxidation on perovskites (*i.e.*, below 573 K) [52], [63], [85] by following a Langmuir-Hinshelwood type mechanism [86], [87]. It is also known that CO oxidation on perovskites is enhanced by adsorbed oxygen species ( $O_2^-$ ,  $O_2^{2-}$  or  $O^-$ ) [88], [89]. On the other hand, alternative studies claim that Mars-van Krevelen-type mechanism can also be the main path for CO oxidation on perovskite systems where oxygen vacancies are formed at elevated temperatures [87], [90]. Whereas, formation of oxygen vacancies is strongly correlated to the connected to the redox capability of the B-site cations. Catalytically important B sites in  $LaCoO_3$  and  $LaMnO_3$  can acquire a variety of oxidation states, such as  $B^{4+,3+,2+,0}$  in a reversible manner, when they are exposed to oxidizing or reducing environments initiating catalytic conversion [32], [91], [92]. However, it is also possible to have irreversible redox processes, which can lead to catalytic deterioration and activity loss.

The structural modifications of the perovskite structure by using different A-site and/or B-site cations can result in the emergence of structural defects enhancing catalytic activity without the collapse of the perovskite lattice. Non-stoichiometric perovskite structures [44], [52], [54], [82], [83], [93] and the correlation between catalytic activity and cationic substitutions have been studied extensively in the literature. These non-stoichiometric perovskite materials maintain their electrical neutrality by altering their B-site oxidation

states. The defects in the perovskite systems can boost NO/CO oxidation performance and oxygen mobility [32], [91], [92], [94]. Former studies showed that La based single B-site (B = first row transition metal)  $\text{LaBO}_3$  type perovskites containing Mn or Co can be utilized as PGM-free catalytic architectures to oxidize NO and CO [32], [95].

However, designing catalytic materials where the catalytic functionality can be gradually modified in a controlled manner is a challenging task. Along these lines, Co and Mn containing perovskite systems offer promising catalytic opportunities in a variety of catalytic oxidation, reduction [96], [97] and coupling [98], [99] reactions thanks to their dynamic redox properties and fine-tunable chemical/surface/electronic structures. Furthermore, Co and Mn incorporation in the B-sites of the perovskite-based materials have a potential to offer reversible redox properties vital for catalytic regeneration. It was reported that populating  $e_g$  electronic levels of B-site cations with electrons by 50-100% is crucial to promote CO/NO oxidation performance [44], [45], [100] and oxygen reduction reaction (ORR) [45], [101]. Such density of states corresponds to a B-site oxidation state of  $+3 < x < +4$  enhancing catalytic performance. The fundamental reasons behind the catalytic function of PGM-free perovskites and associated catalytic mechanistic steps are still unclear [44], [52], [54], [82], [83].

In the current work, novel  $\text{La}_x\text{Co}_y\text{Mn}_z\text{O}_{3+\alpha}$  type B-site mixed perovskite materials are synthesized. Incorporation of Co and Mn led to superior catalytic CO oxidation and NO oxidation with  $\text{O}_2$ . Our findings indicate that the crystal structure, specific surface area (SSA), oxidation state of B-site cations, oxygen vacancy population, oxygen vacancy mobility, and the redox reversibility of the B-site cations under repeated oxidation/reduction cycles can be fine-tuned. Based on the comprehensive *in-situ/ex-situ* spectroscopy, microscopy, and diffraction experiments, detailed electronic, chemical, crystallographic, and morphological properties of the  $\text{La}_x\text{Co}_y\text{Mn}_z\text{O}_{3+\alpha}$  systems are elucidated. Current results demonstrate that the B-site mixed perovskite systems reveal higher catalytic activity as compared to PGM based conventional catalytic systems even at severe reaction conditions. The origin of catalytic performance of these perovskites can be linked to their unique: i) bulk oxygen vacancy population, ii) enhanced redox reversibility,

iii) superior mobility of oxygen vacancies (*i.e.*, oxygen vacancy shuttling between bulk and surface), and iv) bulk stoichiometry of B-site cations.

#### **1.4.2. Fe and/or Co on CeO<sub>2</sub>-ZrO<sub>2</sub> Based NO<sub>x</sub> Reduction Catalysts**

Partial reduction of the metal oxide support (*i.e.*, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>) in the presence of H<sub>2</sub>(g) leading to enclosure and covering of the metal nanoparticles (NPs) is commonly referred as the strong metal support interaction (SMSI) [102]. The synthesis of metal supported catalysts enables anchoring of active metal sites on the support offering enhanced dispersion of active metal sites and improved thermal stability of the metals against sintering [103], [104]. Formation of support oxide over layers on metal NPs can either suppress [105] or boost [106] the catalytic activity of the catalysts. SMSI can be exploited to control NP shape and electronic structure. An analogous concept called the electronic metal support interaction (EMSI) targets activity improvement via electronic modification of the metallic active sites via charge transfer between the metal and the reducible support material [107], [108].

Metal oxide supported catalysts have been utilized for various reactions such as dehydrogenation, polymerization, and particularly selective catalytic reduction (SCR) reactions for NO<sub>x</sub> removal in the presence of ammonia [109]–[111]. Such metal oxides have been used to enhance specific surface area and sinter resistance of active metal sites via SMSI [104], [107], [112]. On the other hand, EMSI between metal-support interface is another crucial factor that can facilitate catalytic activity by dictating the adsorption properties of reactants and poisoning characteristics of adsorption sites [104], [107], [110]–[113]. Among various metal oxides, CeO<sub>2</sub> is considered to be one of the most efficient support materials [114]–[119] in NO reduction due to its redox properties, oxygen storage capacity, vacancy population, and vacancy mobility.

About 0.0046 wt. % of the Earth's crust is comprised of elemental cerium [120]. As can be seen in **Figure 1-6**, utilization of ceria in various research applications, particularly in the field of catalysis has been constantly increasing in the last decades.

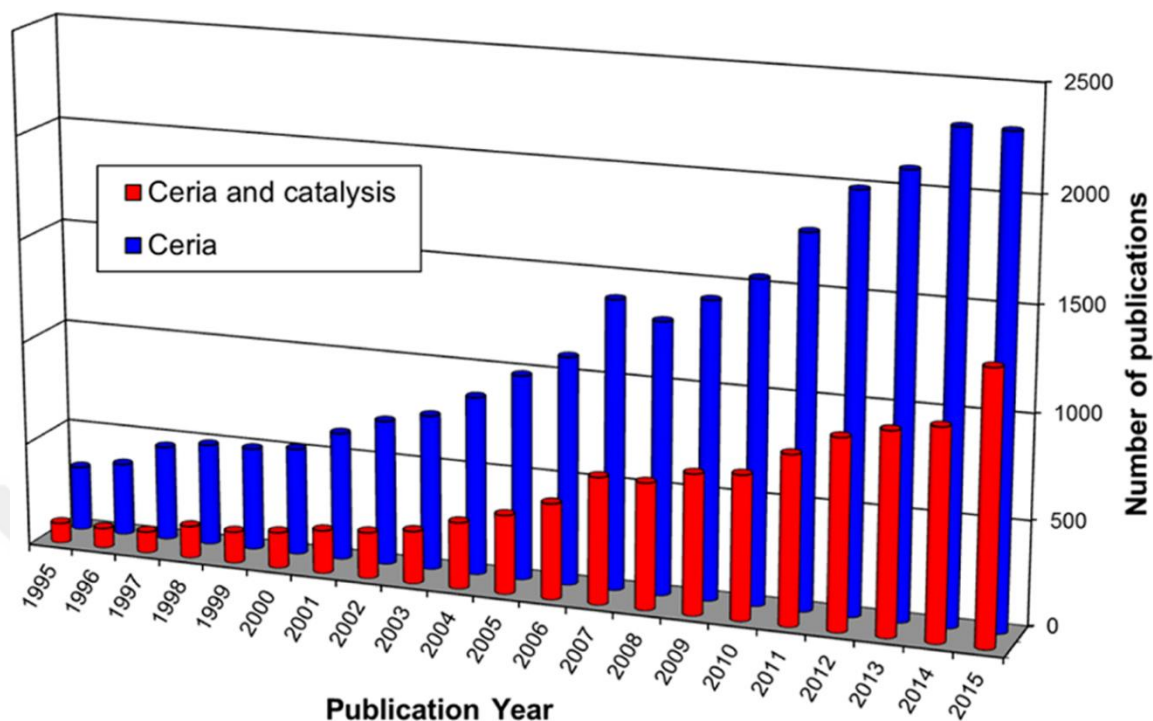
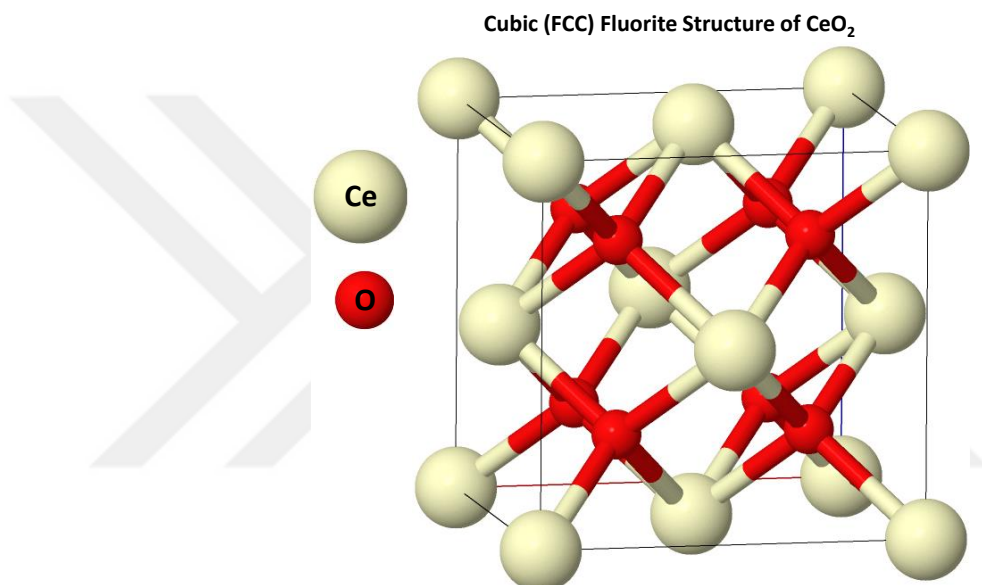


**Figure 1-6.** Number of publications related with Ceria (blue bars) and publications related with ceria and catalysis (red bars) from 1994-2015 [121]. Copyright (2020) American Chemical Society.

CeO<sub>2</sub> has a calcium fluorite crystal structure (see **Scheme 1-5**), and this structure consists of a cubic (FCC) close packed array of cerium cations along with oxide ions occupying tetrahedral holes. The spontaneous formation of Ce<sup>3+</sup> ( $\Delta G^{\circ}_{298} = -1796$  kJ/mol) can distort CeO<sub>2</sub> crystal structure or create entirely different Ce<sub>2</sub>O<sub>3</sub> crystal structure because of the reduction of Ce<sup>4+</sup> ( $\Delta G^{\circ}_{298} = -1089$  kJ/mol) cations to Ce<sup>3+</sup> [121]. In the presence of a reducing agent such as H<sub>2</sub> and particularly at elevated temperatures, CeO<sub>2</sub> may become oxygen deficient, and acquire a non-stoichiometric CeO<sub>2-x</sub> form [122]–[124]. The quantification of “x” in the CeO<sub>2-x</sub> structure with XRD may not be trivial [121]. Therefore, the phase distribution of Ce<sub>2</sub>O<sub>3</sub> (Ce<sup>3+</sup>)-CeO<sub>2</sub>-(Ce<sup>4+</sup>) can be monitored via electron or neutron diffraction methods [125], [126]. Under oxygen deficient conditions and at temperatures above 958 K, CeO<sub>2</sub> may transform into non-stoichiometric CeO<sub>2-x</sub> where x can be within  $0 < x < 0.29$  [121]. High temperature XRD results demonstrate that the lattice parameter “a” for the cubic structure increases as a function of increasing Ce<sup>3+</sup> population in the lattice, since Ce<sup>3+</sup> has a higher ionic radius than Ce<sup>4+</sup> [127], [128]. Former temperature programmed reduction (TPR) experiments indicated [129] the reduction of surface oxygens of CeO<sub>2</sub> with hydrogen at 770 K, while bulk reduction of CeO<sub>2</sub> to yield

$\text{Ce}_2\text{O}_3$  was observed at 1100 K.  $\text{CeO}_2$  reduction with  $\text{H}_2$  can be examined in four successive steps [130]:

- 1- Dissociation of  $\text{H}_2$  on ceria and the formation of surface hydroxyl groups
- 2- Formation of oxygen vacancies and reduction of adjacent cations
- 3- Water desorption due to the recombination of hydrogen and hydroxyl groups
- 4- Oxygen vacancy diffusion from surface to bulk



**Scheme 1-5.** Representation of the crystal lattice cubic (FCC)  $\text{CeO}_2$  unit cell.

Ceria reduction starts on the surface and bulk reduction only begins after all surface sites are reduced. Surface reduction of ceria involves not only oxygen desorption from the surface but also diffusion of oxide ions to the bulk with the formation of vacancies on the ceria surface [131]–[134]. The  $\text{H}_2$  treatment of  $\text{CeO}_2$  leads to an increase in the formation of hydroxyl groups particularly with increasing the reduction temperature up to 673 K [134]–[136]. At higher temperatures dehydroxylation due to water desorption is observed. Bernal *et al.* [137], [138] showed that on  $\text{CeO}_2$  and  $\text{Rh/CeO}_2$  surfaces, transition between  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  states can be achieved in a rather reversible manner under various oxidizing/reducing conditions. Formation of oxygen vacancies on ceria can also be monitored via  $\text{O}_2$  adsorption on ceria. Oxygen adsorption can also provide insight regarding the key intermediates that can be formed during the oxidation/reduction of  $\text{CeO}_2$ . In addition, on the reduced ceria surfaces, formation of superoxide  $\text{O}_2^-$  and peroxide  $\text{O}^-$

species could also be monitored in the oxygen adsorption experiments. Formation of superoxide and peroxide species upon  $O_2$  adsorption on reduced ceria surfaces yields IR bands at  $1124\text{ cm}^{-1}$  and  $883\text{ cm}^{-1}$  [139]–[143]. The oxygen vacancy formation and  $H_2$  activation processes are vital for NO reduction on ceria. Formation of lattice vacancies in ceria are useful in NO reduction as they can form  $N_2O$ , which can eventually boost  $N_2$  production [144]. Interestingly, even after a significant amount of oxygen loss from the ceria lattice,  $CeO_2$  can still preserve its fluorite crystal structure and can be readily regenerated after an oxidation treatment [122], [135]. The reversible redox characteristics of ceria and its reversible oxygen mobility are the key for the structural durability of ceria-based systems in catalysis applications.

Structural and functional enhancement of ceria with secondary metal oxides or secondary metals is also possible. Various studies investigated the interaction of metal functionalized  $CeO_2$  with oxygen [145]–[152]. For instance, it was reported that calcination of  $Pt/CeO_2$  in the presence of oxygen at elevated temperatures resulted in Pt oxidation and formation of Pt-O bonds which stabilized dispersion of Pt species on ceria [148], [150], [151], [153]. Higher Pt loadings on ceria was found to result in rapid sintering of Pt species at high temperatures [154]. Thus, it was shown that by carefully controlling the metal loading, uniformly distributed Pt species can be formed on ceria. In a former study, it was shown that on a  $Pt/CeO_2$  catalyst revealing high activity in  $CO + NO$  reaction, ceria domains covered Pt sites and generated new catalytic active sites for NO conversion [155]. Additional studies also indicated that the formation of reduced  $Ce^{3+}$  sites incorporated with Pd and Pt at the metal-metal oxide interface enhanced CO and/or  $CO_2$  activation and enabled reversible transport of oxygen species between metal (Pt, Pd) and the metal oxide support (ceria) surfaces [156]–[158].

Zr incorporation to ceria has been widely studied to improve oxidation capability, thermal stability, and sintering resistance of TWC-based emission control systems [159]–[162]. Zr incorporated  $CeO_2$  systems may result in a dramatic increase in oxygen storage capacity (OSC) [163]–[165]. In a former report, it was illustrated that the oxygen storage capacity of pure ceria is restricted by the total number of surface oxygens while Ce-Zr mixed oxide systems can also utilize bulk oxygen sites for total oxygen storage [163]. Similar behavior

was also verified via EXAFS studies on Ce-Zr mixed metal oxide mixtures, where the shorter Ce-O bond length was observed to elongate in the presence of Zr-O linkages suggesting a weaker metal oxygen bonding leading to a higher oxygen mobility and enhanced reversibility of oxygen diffusion in the Ce-Zr mixed oxide lattice which ultimately improved catalytic functionality [166]–[168].

The use of ZSM-5 or SSM-13 zeolites as a support material were attempted to increase DeNO<sub>x</sub> efficiency in NH<sub>3</sub>-SCR systems [169], [170]. However, insufficient durability of ZSM-5 and SSM-13 against hydrothermal aging restricts the lifetime of the catalyst due to the suppression of NO reduction capability [169]–[171]. In this work, instead of ZSM-5 or SSM-13 materials, CeO<sub>2</sub> based support materials were functionalized with Fe and/or Co to develop a material with higher NO reduction ability and higher thermal durability. While hydrothermal stability of the synthesized Fe-Co/CeO<sub>2</sub> systems were not studied in the current work, their NO reduction performance was benchmarked against a PGM-catalyst with a superior NO reduction capability than that of zeolite-base catalysts.

### 1.4.3. NO<sub>x</sub> and SO<sub>x</sub> Coordination Chemistry

The oxidative catalytic conversion of NO<sub>x</sub> species may lead to the formation of nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), nitrosyls, and dinitrosyl species on the catalyst surface. Detection of these species with *in-situ* vibrational spectroscopy is essential to account for their higher catalytic activity. **Table 1-2** demonstrates the symmetry alteration of NO<sub>x</sub> species as a function of adsorption geometry. Here, vibrational frequencies were taken from Ref [172]. IR and Raman active modes were separately presented to indicate splitting of IR and/or Raman modes as a result of the lowered symmetry of adsorbed species. Free nitrate ion has a D<sub>3h</sub> symmetry (**Table 1-2**) with the corresponding principal symmetry operators of *E*, *C*<sub>3</sub>, *C*<sub>2</sub>, *σ*<sub>h</sub>, *σ*<sub>v</sub> and *S*<sub>3</sub>. There are 6 vibrational modes available for the free nitrate ion (*2E'*, *A*<sub>1</sub><sup>'</sup>, and *A*<sub>2</sub><sup>''</sup>) where *E'* mode is doubly degenerate. Vibrational frequencies of these modes are 720 (*E'*), 831 (*A*<sub>2</sub><sup>''</sup>), 1390 (*E'*) and 1050 (*A*<sub>1</sub><sup>'</sup>) cm<sup>-1</sup> [173]. Due to no dipole moment change of *A*<sub>1</sub><sup>'</sup> (1050 cm<sup>-1</sup>) mode, this mode is not IR active. The coordination of nitrate (NO<sub>3</sub><sup>-</sup>) species to a surface changes its symmetry group from D<sub>3h</sub> to C<sub>2v</sub>. The symmetry lowering results in six IR and six Raman active modes (see **Table 1-2**). In the spectroscopic studies,

all IR modes may not be visible due to experimental limitations (*e.g.*, due to the limited transparency of the spectroscopic optical components at certain frequencies) [173].

Adsorption of nitrite ( $\text{NO}_2^-$ ) may not always lower the symmetry (see **Table 1-2**) for particular adsorption geometries. However, monodentate adsorption through the O atom (see **Table 1-2**) lowers the symmetry from  $C_{2v}$  to  $C_s$ . The  $B_1$  mode is vanished in both IR and Raman peaks.

**Table 1-2.** The symmetry comparison of adsorbed and free  $\text{NO}_x$  species adapted from [172].

| Structure                                                                            | $\nu_3$ (cm <sup>-1</sup> ) |           | $\nu_1$ (cm <sup>-1</sup> )    | Point Group     | Ir Active Modes                                             | Raman Active Modes                                                                   |
|--------------------------------------------------------------------------------------|-----------------------------|-----------|--------------------------------|-----------------|-------------------------------------------------------------|--------------------------------------------------------------------------------------|
| NO <sub>3</sub> <sup>-</sup>                                                         | 1380                        |           | 1050 <sup>a</sup>              | D <sub>3h</sub> | A <sub>2</sub> <sup>-</sup> , 2E <sup>-</sup> (3 Peak)      | A <sub>1</sub> <sup>-</sup> , A <sub>2</sub> <sup>-</sup> , 2E <sup>-</sup> (4 Peak) |
| M—O—N $\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ | 1530–1480                   | 1290–1250 | 1035–970                       | C <sub>2v</sub> | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak) | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak)                          |
| M $\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ NO  | 1565–1500                   | 1300–1260 | 1040–1010                      | C <sub>2v</sub> | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak) | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak)                          |
| M—O $\begin{smallmatrix} \diagup \text{NO} \\ \diagdown \text{NO} \end{smallmatrix}$ | 1650–1600                   | 1225–1170 | 1030–1000                      | C <sub>2v</sub> | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak) | 3A <sub>1</sub> , 2B <sub>1</sub> , B <sub>2</sub> (6 Peak)                          |
| Structure                                                                            | $\nu_s$ (cm <sup>-1</sup> ) |           | $\nu_{as}$ (cm <sup>-1</sup> ) |                 |                                                             |                                                                                      |
| NO <sub>2</sub> <sup>-</sup>                                                         | 1260                        |           | 1330                           | C <sub>2v</sub> | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                   | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                                            |
| M—O $\begin{smallmatrix} \diagup \text{N} \\ \diagdown \end{smallmatrix}$            | 1220–1205                   |           |                                | C <sub>2v</sub> | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                   | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                                            |
| M—N $\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$   | 1440–1335                   |           | 1350–1315                      | C <sub>2v</sub> | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                   | 2A <sub>1</sub> , B <sub>1</sub> (3 Peak)                                            |
| M—O—N=O                                                                              | 1470–1450                   |           | 1065–1050                      | C <sub>s</sub>  | 3A <sub>1</sub> (3 Peak)                                    | 3A <sub>1</sub> (3 Peak)                                                             |
| M—O $\begin{smallmatrix}   \\ \text{M}-\text{N}-\text{O} \end{smallmatrix}$          | 1520–1390                   |           | 1260–1180                      | C <sub>s</sub>  | 3A <sub>1</sub> (3 Peak)                                    | 3A <sub>1</sub> (3 Peak)                                                             |

<sup>a</sup>Forbidden in the IR spectrum.

$\text{SO}_x$  species commonly present in the  $\text{DeNO}_x$  aftertreatment systems can easily poison the catalysts and result in catalyst deactivation. Therefore, adsorption properties of  $\text{SO}_x$  species are important to provide fundamental insights about the poisoning mechanism. IR active modes of free sulfate ( $\text{SO}_4^{2-}$ ) ions are due to the  $T_2$  symmetry. However, adsorption of sulfate ions to surfaces may lower the symmetry of free sulfate ( $\text{SO}_4^{2-}$ ) ions from  $T_2$  to  $C_{3v}$  or  $C_{3v}$ , increasing the number of active IR modes (see **Table 1-3**).

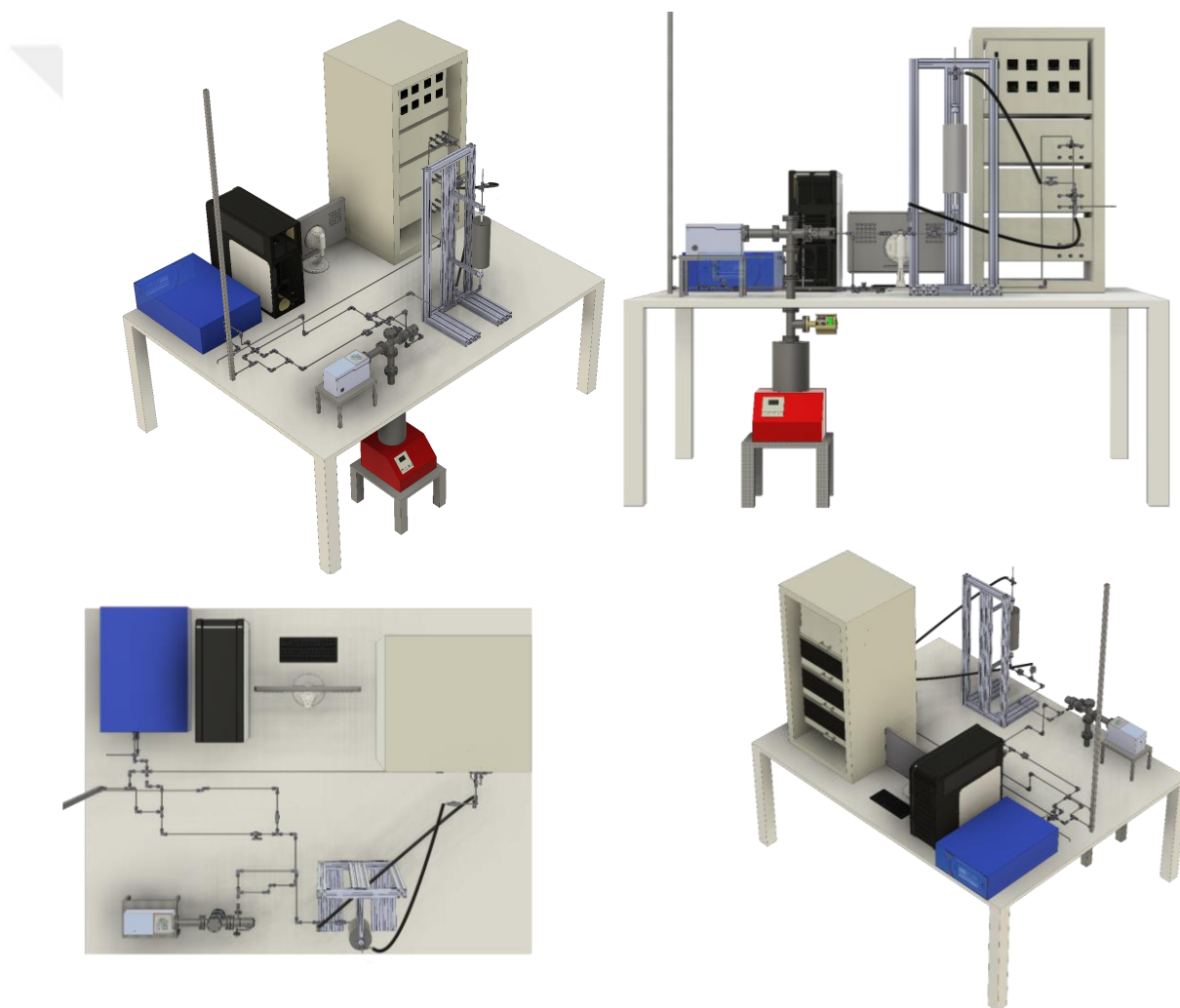
**Table 1-3.** The symmetry comparison of adsorbed and free  $\text{SO}_x$  species adapted from [172].

| Compound or ion                          | Symmetry | $\nu_1$ ( $\text{cm}^{-1}$ ) | $\nu_3$ ( $\text{cm}^{-1}$ ) | Raman Modes                      | IR modes                    |
|------------------------------------------|----------|------------------------------|------------------------------|----------------------------------|-----------------------------|
| $\text{SO}_4^{2-}$ (free ion)            | $T_d$    | 983                          | 1105                         | $A_1, E, 2T_2$ (4 peak)          | $2T_2$ (2 peak)             |
| $\text{SO}_4^{2-}$ (monodentate complex) | $C_{3v}$ | 970                          | 1032–1044, 1117–1143         | $3A_1, 3E$ (6 peak)              | $3A_1, 3E$ (6 peak)         |
| $\text{SO}_4^{2-}$ (bidentate complex)   | $C_{2v}$ | 995                          | 1050–1060, 1170, 1105        | $4A_1, A_2, 2B_1, 2B_2$ (9 Peak) | $4A_1, 2B_1, 2B_2$ (8 Peak) |

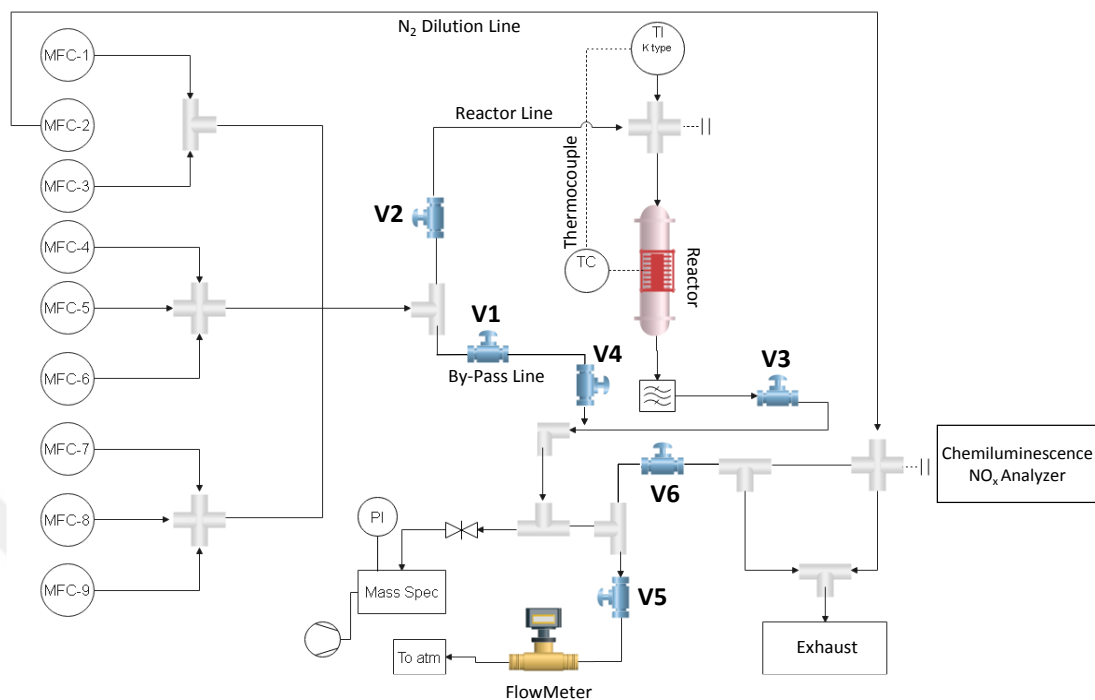
## CHAPTER 2

### 2. Flow Reactor Design

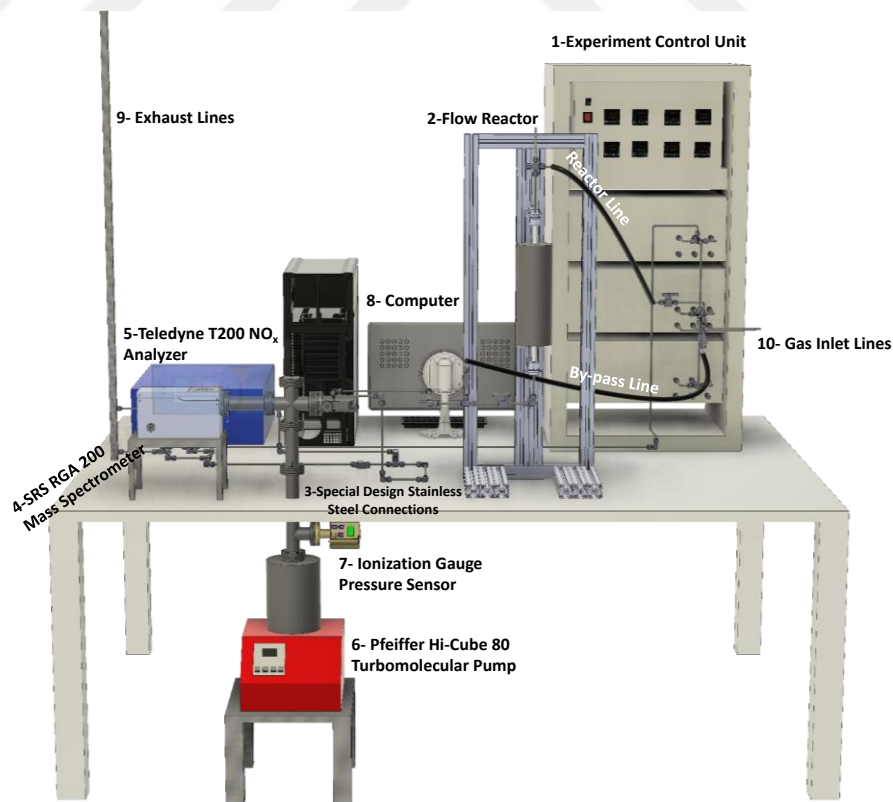
The catalytic performance tests performed in the current work were carried out using a custom design flow mode reactor which was also designed and constructed as a part of the current thesis. The schematic representation and the main components of the flow reactor are given in *Scheme 2-1* to *2-4*.



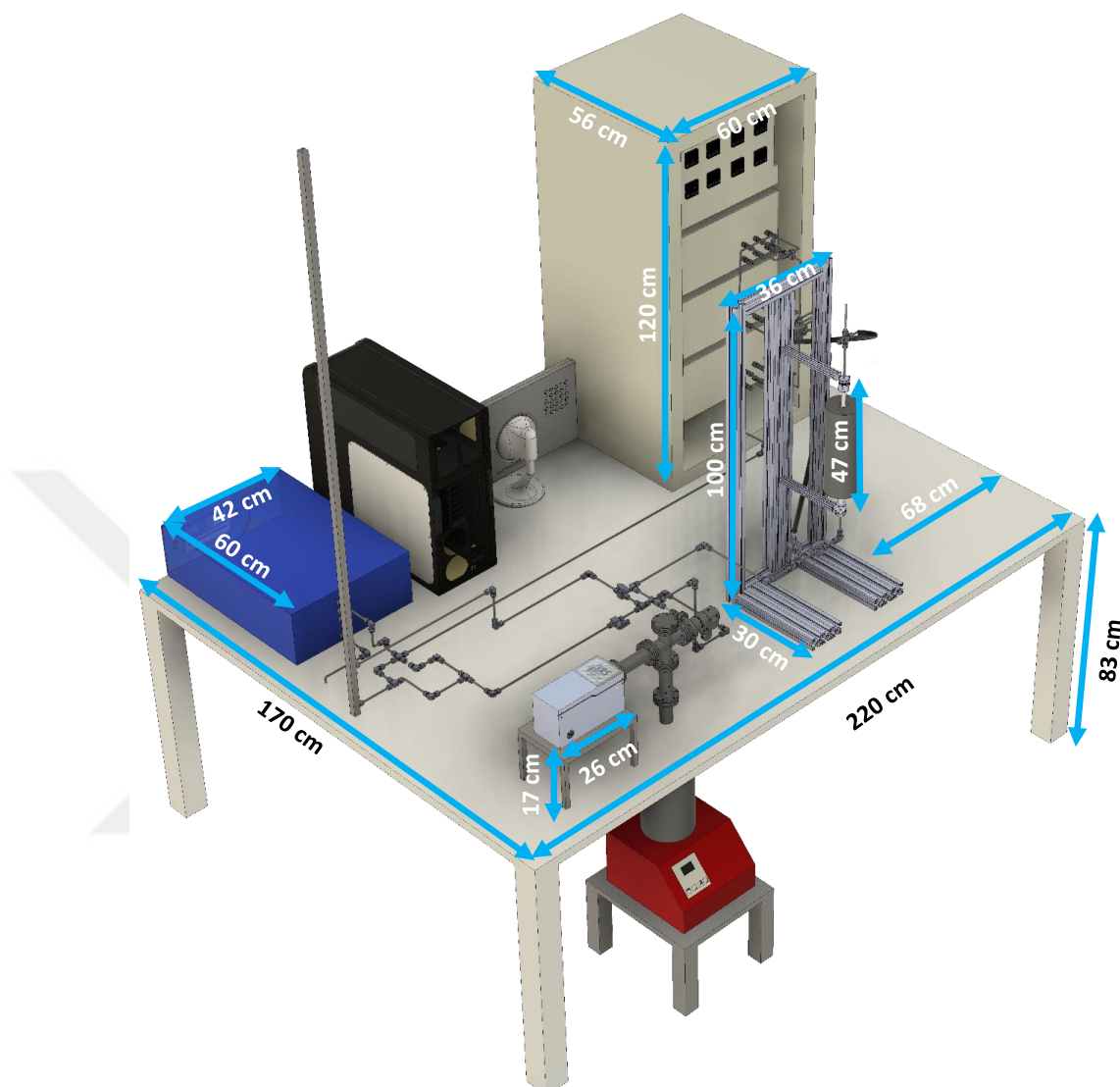
*Scheme 2-1.* General view of the custom-design flow reactor setup used in the catalytic performance tests.



**Scheme 2-2.** Operational 2D drawing of flow reactor diagram.



**Scheme 2-3.** Main functional components of the catalytic flow reactor.



**Scheme 2-4.** Basic dimensions of the functional components of the flow reactor.

The main components of the flow reactor will be described in more detail in the forthcoming section. These components and their basic definitions are listed below:

- 1- **Experiment Control Unit:** The experiment control unit consists of 9 different Mass Flow Controllers (MFC) with Hastings® HFC-202 model number and Proportion Integration Derivation (PID) controllers for controlling the reactor and gas line temperatures.
- 2- **Flow Reactor:** A quartz tube with a node, resistor, and a thermal insulation jacket.
- 3- **Custom-made Stainless-Steel Connections:** Airtight Swagelok® and Conflat® connections were utilized to restrict the leakage of toxic and dangerous gas streams ( $10^{-11}$  - 3 bar) used in the experiments.

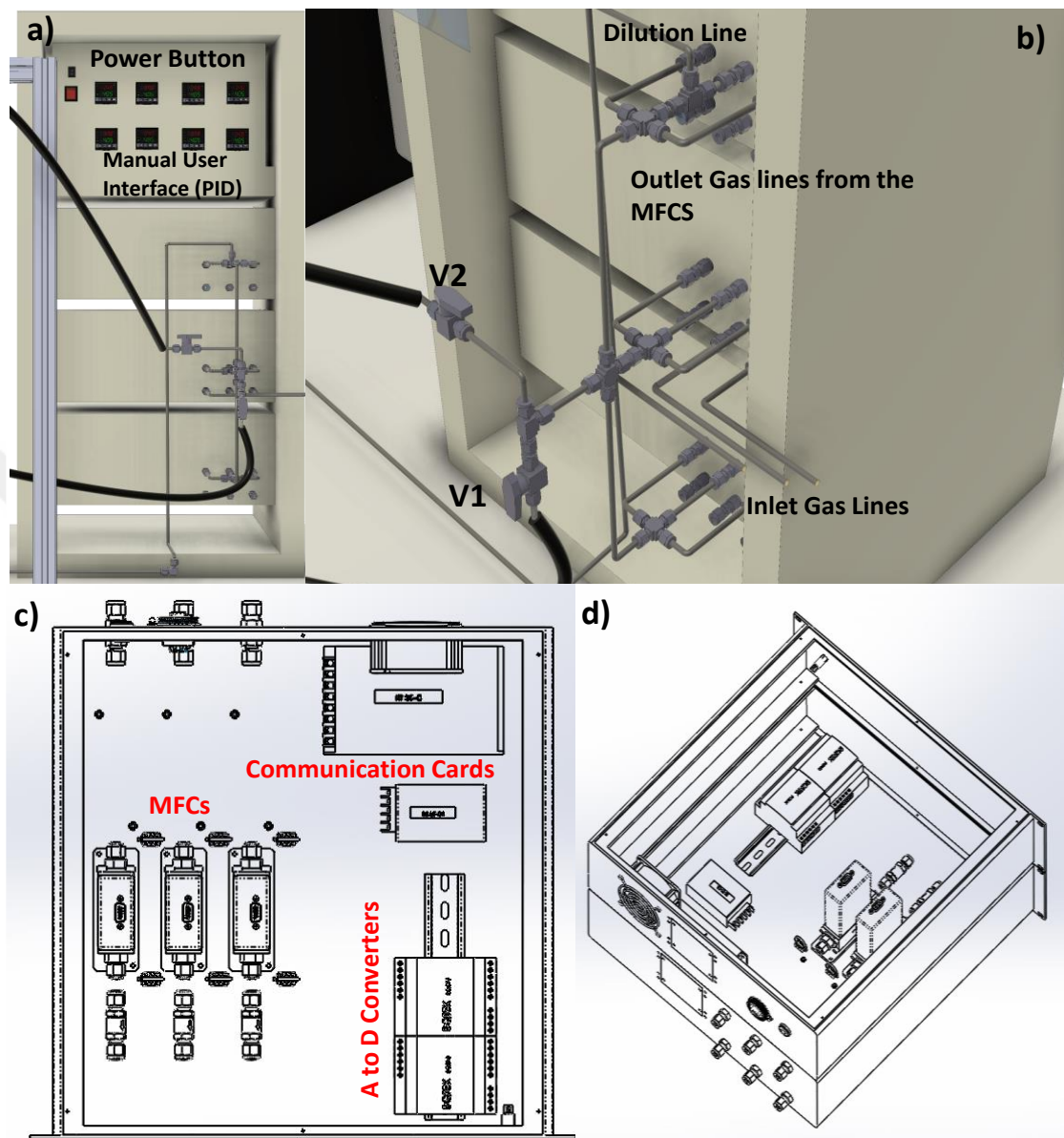
- 4- **SRS RGA 200:** On-line Stanford Research Systems (SRS) Residual Gas Analyzer (RGA) 200 (operational within 0-200 amu) quadrupole mass spectrometer (QMS) located in the flow reactor enables monitoring of reactants and products in real-time.
- 5- **Teledyne T200 NO<sub>x</sub> Analyzer:** Chemiluminescence NO<sub>x</sub> analyzer provides real-time detection of NO and NO<sub>2</sub> concentrations in the reactor downstream.
- 6- **Pfeiffer Hi-Cube 80 Turbomolecular Pump:** Turbomolecular and diaphragm pump combination providing pumping of the QMS chamber from 1 bar to 10<sup>-11</sup> bar.
- 7- **Ionization Gauge Pressure Sensor:** Bayard Alpert-type hot filament ionization gauge used to measure the high vacuum in the QMS chamber (10<sup>-6</sup> - 10<sup>-11</sup> bar).
- 8- **Computer:** Different commercial and custom-design software packages are used to control/operate sensors, spectrometers, valves, MFCs, and PIDs located in the flow reactor.
- 9- **Exhaust Lines:** 1/4" stainless steel (SS) tubing utilized to remove toxic reactants and/or products in the reactor downstream.
- 10- **Gas inlet Lines:** 1/4" SS tubing transferring pressurized (3 bar(g)) reactant gases from the gas cylinders to the reactor.

Each functional component of the custom-design flow reactor was carefully optimized to perform catalytic experiments with reproducible and accurate results. Basic considerations in the experimental design of the flow mode catalytic performance tests, standard protocols used prior to/during the experiments are described in detail in the next sections.

## **2.1. Main Components of The Flow Reactor and Their Operational Roles in Flow-mode Catalytic Performance Tests**

### **2.1.1. Experimental Control Unit**

Experimental control unit is comprised of MFCs and PID controllers regulating the gas flow rates, temperatures, and pressures of different sections of the flow reactor. Additionally, the analog to digital converters (ADCs), Solid State Relays (SSRs, for electrical current regulation), and corresponding power supplies are also located in the experimental control unit (see *Scheme 2-3*).

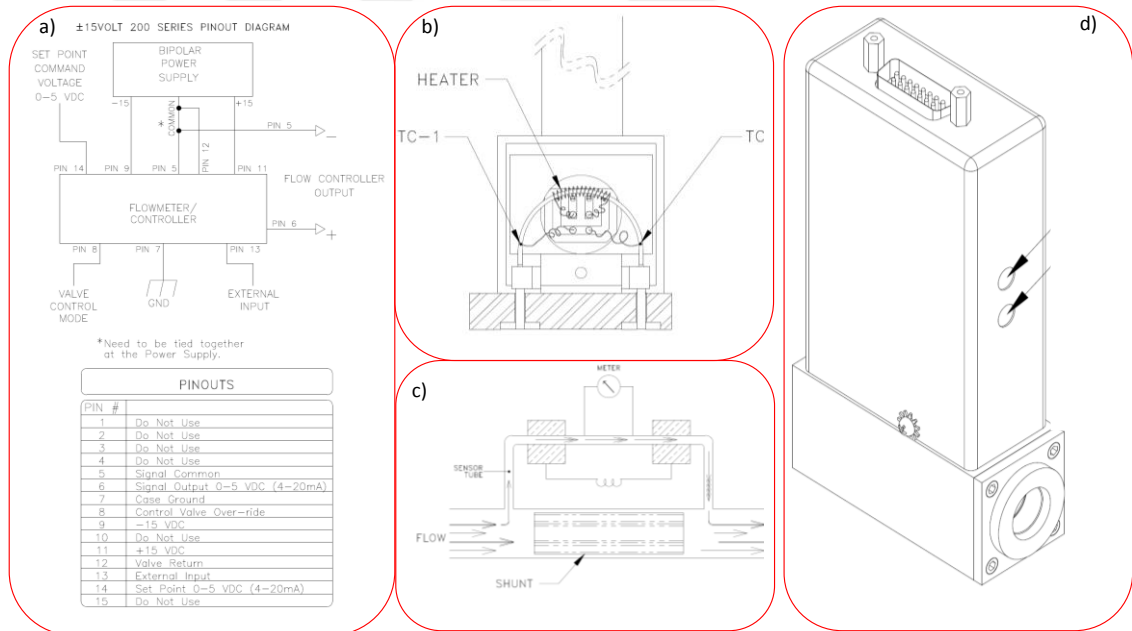


**Scheme 2-5.** The experimental control unit a) overall view of the unit, b) inlet and outlet gas lines of MFCs, c)-d) MFC units.

Two different power buttons are included (red and black power buttons in **Scheme 2-5a**) to separate and protect MFCs, PIDs and their associated electronics. The function of the red power button is to switch on/off the power of the reactor heating and heating of the gas lines while the black power button energizes the sensitive electronics running MFCs and PID controllers and was connected to an Uninterrupted Power Supply (UPS) line. The reactor and gas line heaters were connected to the main power grid due to high-energy demand of these lines that may damage/deplete the UPS power in case of a main grid power

outage. Hence, UPS is only used to protect the sensitive electronic devices embedded in the experiment control unit from power disruptions.

MFCs are among the most critical subcomponents of the flow reactor system, which control the flow rate of gases and gas mixtures passing through the catalytic reactor during the performance tests. There are three identical boxes in the flow reactor system each of which contains 3 separate MFC units (**Schemes 2-5a-5d**). Thus, a total of 9 MFCs are utilized in the flow reactor system where 8 of these MFCs are connected through 1/4" SS tubing lines via Swagelok tees or cross unions (**Scheme 2-5b**). The 9<sup>th</sup> MFC output line is separated from others so that it can be used for the dilution of the input line for Teledyne T200 NO<sub>x</sub> analyzer. V1 and V2 are bypass valves (**Scheme 2-2**). These valves can be used to divert flows of 8 different MFCs from the reactor to the exhaust.



**Scheme 2-6.** Detailed structural and functional description of an MFC unit. a) Circuit view, b) inner view, c) flow scheme, and d) outer casing. Adapted from Ref [174].

The total gas flow rate in the reactor and pipelines is calculated by summing individual flow rates of MFCs which are listed in **Table 2-1**. The detailed structural and functional description of an MFC is given in **Scheme 2-6**. HFC-202 MFCs work with 15 VDC (Volt, Direct Current) power supply (**Scheme 2-6a**). The flow rate scale of the corresponding MFC is determined by 0-5 VDC analog signal (**Scheme 2-6a**) where a 0 to 5 VDC feedback signal is also generated by the corresponding MFC to verify the flow rate. The main

components of an MFC include a sensor, a shunt and a valve (**Schemes 2-6b-c**). The thermocouple (TC) in the MFC (**Scheme 2-6b**) determines temperature of the gas in the entrance and end of the MFC. The flow rate of the MFC at the sensor can be maximum 10 sccm (standard cubic centimeter) [174] which is a precise fraction of the total flow passing through shunt (**Scheme 2-6c**). The operational principle of an MFC can be explained as follows: the TC-1 and TC-2 (see **Scheme 2-6b**) measures the temperature difference of the gas as a function of the flow rate and type of the gas at constant power input by a coil (**Scheme 2-6b**). Then the difference between TC-1 and TC-2 is amplified and converted to an analog signal which determines the opening extent of the valve (shunt, **Scheme 2-6b**) to regulate the gas flow rate. Finally, the temperature difference of TC-1 and TC-2 is converted to an analog signal and compared to the feedback signal coming from the valve as a function of valve opening extent, where valve position can be altered until TC-1 and TC-2 difference signal becomes equal to the feedback signal. The heat capacity of the flowing gas and its flow rate determines the TC-1 and TC-2 temperature difference in the MFC.

**Table 2-1.** Different MFCs used in the flow reactor system and their associated parameters.

| MFCs | Range (SCCM) | Calibration Gases        | GCF (Gas Correction Factor) |
|------|--------------|--------------------------|-----------------------------|
| MFC1 | 0-1500       | Ar                       | 1.385                       |
| MFC2 | 0-3000       | Ar                       | 1.385                       |
| MFC3 | 0-30         | 8% NO/Ar                 | 1.354                       |
| MFC4 | 0-1000       | 4% H <sub>2</sub> /Ar    | 1.379                       |
| MFC5 | 0-500        | O <sub>2</sub>           | 0.979                       |
| MFC6 | 0-200        | CO <sub>2</sub>          | 0.752                       |
| MFC7 | 0-20         | 1% SO <sub>2</sub> /Ar   | 1.387                       |
| MFC8 | 0-400        | 0.5% NO <sub>2</sub> /Ar | 1.395                       |
| MFC9 | 0-300        | 4% NH <sub>3</sub> /Ar   | 1.358                       |

**Table 2-1** Different MFCs located in the experimental control unit and their associated parameters. Each MFC is calibrated with a certain gas under different temperature and pressure conditions (**Scheme 2-7**) such as Standard Temperature and Pressure (STP, 273 K and 1 bar) or Normal Temperature Pressure (NTP/N, 293 K and 1 bar).



**Scheme 2-7.** An MFC casing indicating calibration conditions and MFC specific parameters.

The gas correction factor (GCF) is another crucial parameter for a given MFC (see **Table 2-1**). The main purpose of using a GCF parameter is related to differences in the heat capacities of the gas/gas mixtures used in the MFC. If the gas utilized by the MFC is identical to its calibration gas, then, use of a GCF is no longer necessary. However, an MFC is used with a gas/gas mixture other than its calibration gas, corresponding GCF used to correct the measured flow rate.

Note that GCF values are specific to a given MFC instrument and brand. In general, GCF of  $N_2$  (g) or air is set to 1.000 where other GCFs are determined according to their heat capacities at constant pressure ( $C_p$ ). GCF for an unknown gas X can be determined by dividing the heat capacity of  $N_2$  to that of gas X (i.e.,  $C_{pN_2}/C_{pX} = GCF_X$ ). GCF for gas mixtures can be calculated by utilizing the gas composition along with the corresponding GCF of each gas in the mixture. For instance, for a gas mixture comprised of 40% A(g)

and 60% B(g),  $GCF_{A+B}$  of the gas mixture can be estimated as  $GCF_{A+B} = 0.4 \times GCF_A + 0.6 \times GCF_B$ .

**Table 2-2.** The macro enabled excel table for GCF calculations for Hastings HFC-202 MFCs.

| Gas Mixture GCF & Z-factor calculator                                                                                                      |          |          |          |          |  |
|--------------------------------------------------------------------------------------------------------------------------------------------|----------|----------|----------|----------|--|
| Select Instrument Series                                                                                                                   |          |          |          |          |  |
| <a href="C:\Users\Administrator\Desktop\gcf_tables\GasDataTables.xls">Open C:\Users\Administrator\Desktop\gcf_tables\GasDataTables.xls</a> |          |          |          |          |  |
| Select Gas names and enter %volume for each gas in mixture.                                                                                |          |          |          |          |  |
| Over-write existing gases as required. Set all other %volumes to 0%                                                                        |          |          |          |          |  |
| Mix values given below.                                                                                                                    | 200N2    |          |          |          |  |
| Gas                                                                                                                                        | % volume | GCF      | 25C Dens | Gamma    |  |
| Carbon Dioxide                                                                                                                             | 4.00%    | 0.7430   | 1.7989   | 1.2200   |  |
| Air                                                                                                                                        | 0.00%    | 0.9980   | 1.1850   | 1.4000   |  |
| Carbon Dioxide                                                                                                                             | 0.00%    | 0.7430   | 1.7989   | 1.2200   |  |
| Argon                                                                                                                                      | 96.00%   | 1.4010   | 1.6329   | 1.6600   |  |
| Ethane                                                                                                                                     | 0.00%    | 0.4820   | 1.2291   | 1.1900   |  |
| Helium                                                                                                                                     | 0.00%    | 1.4020   | 0.1636   | 1.6600   |  |
| Argon                                                                                                                                      | 0.00%    | 1.4010   | 1.6329   | 1.6600   |  |
| Argon                                                                                                                                      | 0.00%    | 1.4010   | 1.6329   | 1.6600   |  |
| Boron Trichloride                                                                                                                          | 0.00%    | 0.4426   | 4.7893   | 1.2000   |  |
| Benzene                                                                                                                                    | 0.00%    | 0.3067   | 3.1928   | 1.2000   |  |
| Argon                                                                                                                                      | 0.00%    | 1.4010   | 1.6329   | 1.6600   |  |
| Mix Values                                                                                                                                 |          | Revision | 1.05     | 9/9/2015 |  |
| GCF:                                                                                                                                       |          | 1.3531   |          |          |  |
| 25C Density:                                                                                                                               |          | 1.640    |          |          |  |
| Gamma:                                                                                                                                     |          | 1.642    |          |          |  |

On the other hand, full scale of a given MFC should also be arranged according to the utilized gas type. A  $N_2$ -MFC ( $GCF_{N_2} = 1$ ) factory calibrated for a maximum flow rate of 100 sccm (sccm: standard cubic centimeter) is only capable to provide 70 sccm Ar(g) flow since  $GCF_{Ar} = 1.4$ . The GCF update for Ar(g) ensures that 0-5 VDC signal range and 0-70 sccm flow range are proportionally overlapped. The 0 to 5 VDC range overlaps with 0-100 sccm flow rate range when GCF of  $N_2(g)$  is used. Hence, GCF defines the flow range of the corresponding gas to the corresponding MFC.

It should be also noted that the chemical compatibility of the used gas with the MFC is important. Inert gas (argon, nitrogen, helium etc.) MFCs may not be compatible with

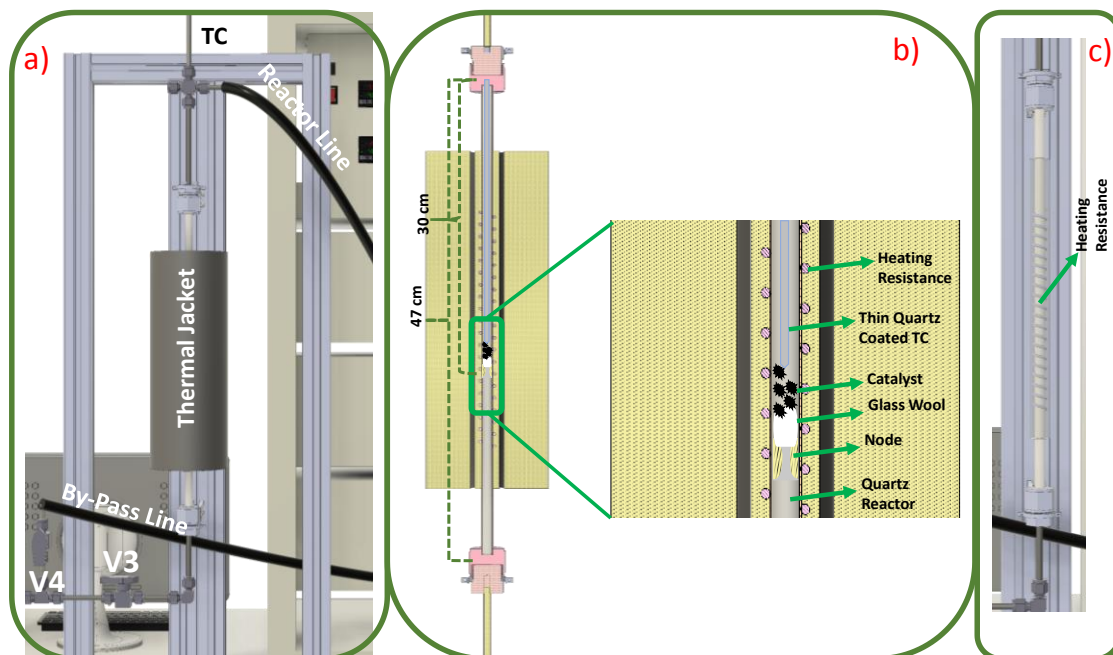
corrosive gases such as NO, CO, NH<sub>3</sub>, SO<sub>2</sub> *etc.* However, the use of inert gases in corrosive gas compatible MFCs is typically not problematic, unless otherwise is recommended by the manufacturer.

The other important subcomponent of the experimental control unit is the PID controllers for temperature control. ORDEL AC441 PIDs are used for controlling the temperature in the heated gas lines, while ORDEL PC441 PID is used for controlling the reactor furnace temperature.

### 2.1.2. Quartz Reactor

A 47 cm long quartz tube with a 1 cm outer diameter, and 0.1 cm wall thickness is used as the reactor (see **Schemes 2-8a-c**) housing powder catalyst samples, where the quartz reactor tube also contained a node at 30<sup>th</sup> cm. Valves labeled as V3 and V4 in **Scheme 2-2** and **Scheme 2-8a** control the flow of the incoming fluid either to the bypass line or to the reactor line. The bypass line is essential to check the presence of any pressure drop in the reactor as well as to perform detector calibration at different gas concentrations/flow rates. Especially, the pressure drop in the presence of a powder catalyst and glass wool (**Scheme 2-8b**) can be a substantial problem to sustain the desired flow rate.

Detailed view of the quartz reactor can be seen in **Scheme 2-8b** along with the node position, heating resistor, glass wool, TC, and the powder catalyst. The sealing of the quartz reactor at both ends is achieved by ½ inch face-sealed VCR connections. Thermocouple inserted into the quartz reactor is a K-type (*Tetcis* brand) TC with a 4 mm outer diameter and 2 mm thickness. TC is also passivated with a quartz coating as Ni-Cr alloys used in the TC can also readily contribute to the catalytic reaction, particularly reduction reactions involving H<sub>2</sub>(g). The heating resistor wrapped outside the quartz reactor can bear a maximum power of 800 W, enabling the heating the reactor from 300 to 1173 K.



**Scheme 2-8.** Detailed description of the quartz reactor a) outer view and connections, b) cross-sectional side view, and c) view without the external thermal insulation jacket.

There are five different control parameters associated with the quartz reactor heating control system which need to be optimized in order to provide stable and sustainable heating control for both linear ramping and soaking temperature regimes. Two of these parameters are (i) Yhll (determining the duration of time where the solid-state relay, SSR, remains ON in a single period) and (ii) Ct (which sets the total duration of the SSR period, *i.e.*, total turn ON + turn OFF time). The main objective to determine Yhll parameter is to optimize the dead band interval (turn off time). The magnitude of Yhll parameter was optimized to keep the total fluctuation less than  $\pm 1$  K during a close watch of reactor temperature at around 573 K. Hence, Yhll time was chosen to be 45 % of the total period for 1 K fluctuation at maximum. Then, period duration (Ct) was also optimized by using the same procedure.

To optimize the remaining three different control parameters (*i.e.*, P, I, and D), the system was heated up to 673 K. Then P parameter was optimized by keeping I and D at zero (*i.e.*, Ziegler-Nichols method [175]). First, P parameters was set to the value, where process value (PV) overshoots the set value (SV) to ensure that P value is enough to reach 673 K. Then, by changing the I parameter, temperature fluctuation was increased which was

compensated by the D parameter to keep the temperature fluctuation at <1 K for both soaking and linear ramping.

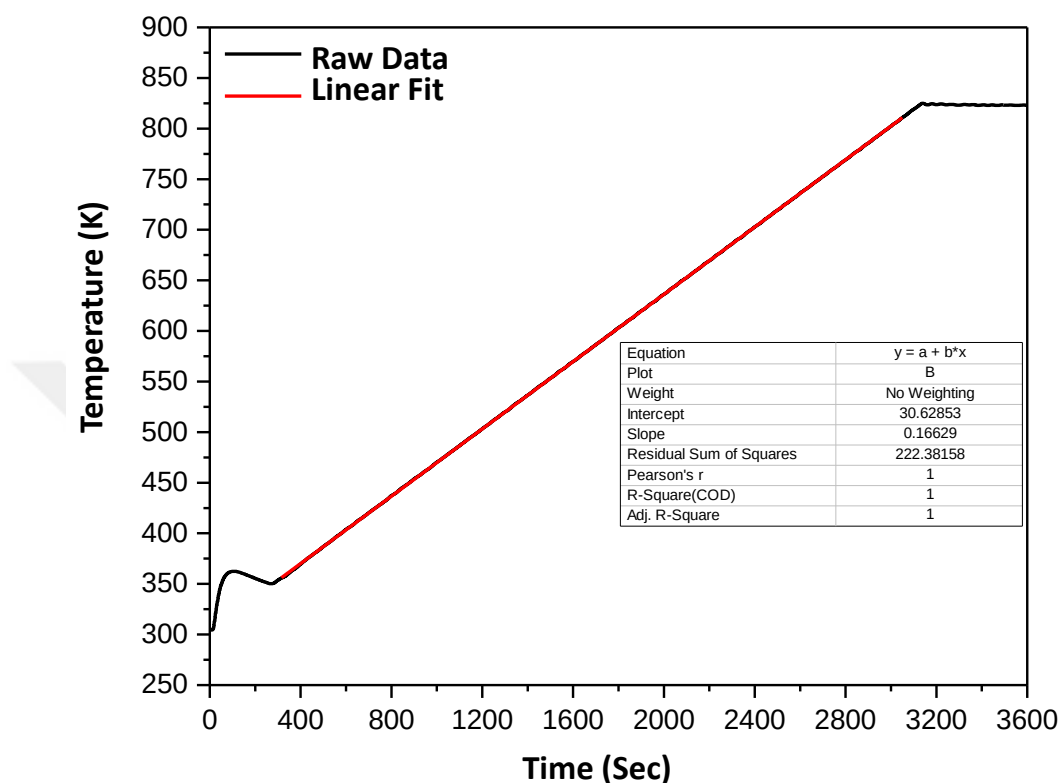


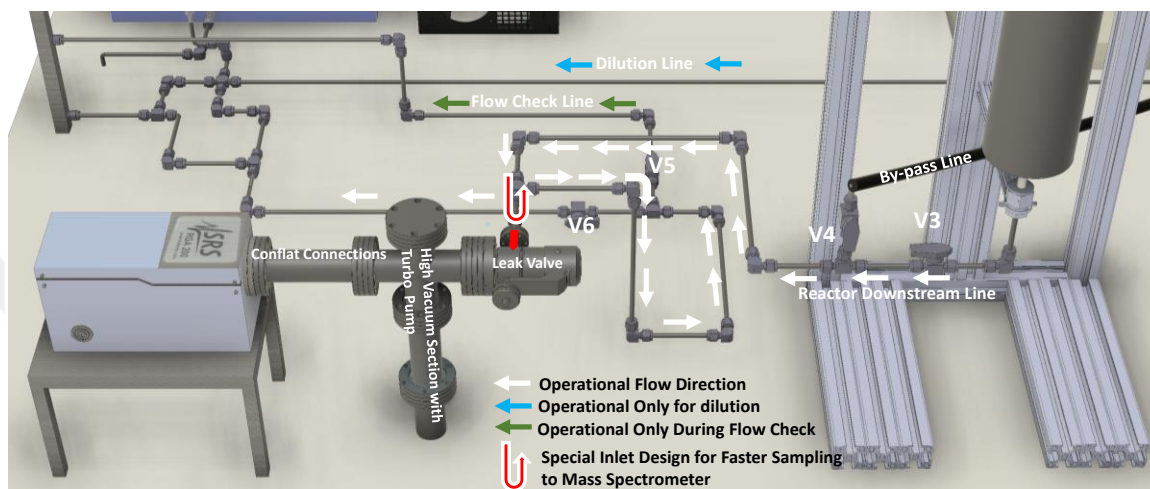
**Figure 2-1.** Linear temperature ramp (10 K/min) and soak at 823 K obtained during a trial experiment for PID optimization.

After optimization of these 5 different reactor temperature control parameters, the reactor furnace was heated up to 823 K with a 10 K/min ramp rate in the presence of 300 sccm Ar(g). **Figure 2-1** shows the heating profile along with the corresponding linear fitting parameters. The linear fitting yields that the slope of the heating ramp is 0.16629 K/sec which corresponds to 9.97 K/min. Therefore, the temperature profile in **Figure 2-1** demonstrates that optimized PID parameters enables very accurate linear temperature control almost entirely suppressing unwanted temperature fluctuations.

### 2.1.3. Special Design Stainless Steel Connections

In the design and construction of the flow reactor system, two major problems were solved associated with the sealing of the pipelines and the gas detection response time in the downstream of the reactor.

The custom design flow reactor includes Swagelok® connections that can be seen in **Scheme 2-9**. Sealing of the gas lines and the reactor is extremely important to ensure safety and also to conduct accurate experiments. Prior to each experiment, a careful leak-test was carried out to ensure the absence of any leaks.



**Scheme 2-9.** Gas stream flow direction and closer demonstration of lok and conflat connections with their operational role during the experiments.

### **Leak Test Protocol**

After the insertion of the catalyst and TC into the quartz reactor as demonstrated in **Scheme 2-8b**, leak test can be carried out by utilizing MFC1 (**Table 2-1**). As shown in **Scheme 2-7**, MFC1 calibration information indicates that upstream pressure of the MFC1 should be 3 bar(g) and the downstream pressure of MFC1 should be 0-1.5 bar(g), respectively. The letter “g” at the end of these pressure designations stands for the so called “gauge pressure” where “0” bar(g) equals to the atmospheric pressure. Therefore, the 1.5 bar(g) downstream and 3 bar(g) upstream calibration pressure of the MFC imply that the gas cylinder and the corresponding MFC connection (upstream) should have maximum 3 bar(g) pressure for accurate flow. The MFC can provide maximum 1.5 bar(g) pressure for the downstream (reactor and pipelines). If the downstream pressure exceeds 1.5 bar(g), the flow rate becomes “0” due to the pressure build up inside the reactor or pipelines.

To perform a leak test, MFC1 flow rate was set to 500 sccm after turning off valves V5-V6 while keeping all other valves on. The purpose of turning off V5-V6 (see **Scheme 2-2** and **Scheme 2-9**) valves is to have a closed system. Then, the flow rate of the MFC1 was monitored for 2-3 min. During this time, all pipelines and the quartz reactor were

pressurized with 1.5 bar(g). After reaching 1.5 bar(g) pressure, the total flow must be “0”. If there is still some flow in the system, it means that there is a leak which should be detected with a soap bubble test.

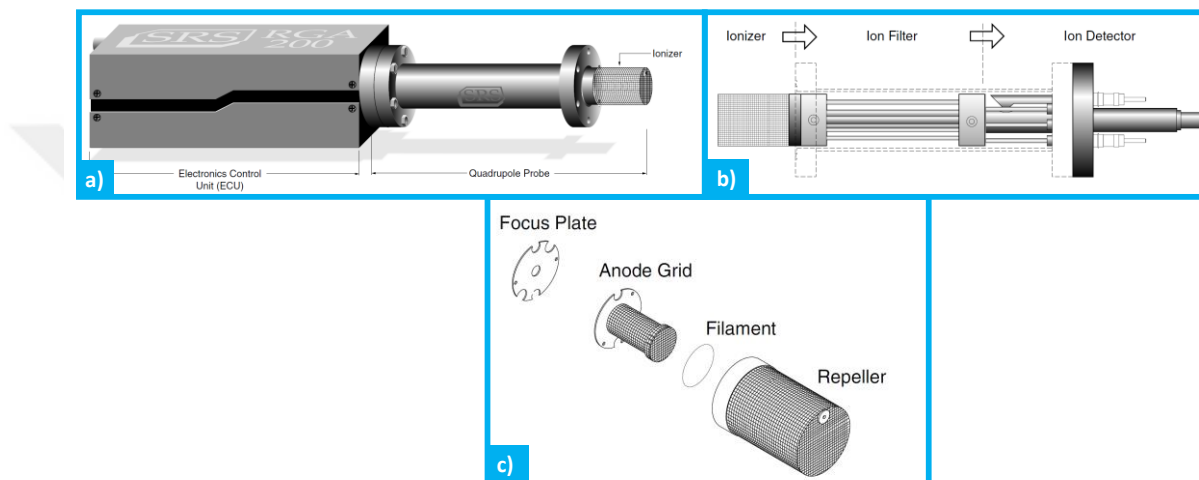
In case that the total flow is found to be zero after 2-3 min, indicating that the system is sealed (*i.e.*, no leaks) at 1.5 bar(g), it is extremely important to remember that pressurizing the reactor is quite dangerous as the quartz reactor is susceptible to rupture at elevated pressures. While SS tubings and fittings used in the flow reactor system are rated for much higher pressures, quartz reactor can resist much lower pressures. Therefore, the maximum pressure durability for the quartz reactor must be calculated by using its outer diameter and thickness. Such calculations [176] indicated that a quartz tube with a 10 mm outer diameter and 1 mm thickness can withstand a maximum of 6.9 bar absolute pressure.

The verification of the flow rate from the bypass and the reactor is another important test in order to detect pressure drops in the reactor or discover MFC failures. Hence, Agilent ADM 200 universal flowmeter with an operational range between 1 to 1000 ml/min, was utilized to cross check MFC flow rates. Since ADM 200 universal flow meter uses a different flow rate unit (*i.e.*, ml/min), it is necessary to convert sccm values of the MFC to actual to ml/min conversion. Assuming that the typical absolute atmospheric pressure in Ankara, Turkey is *ca.* 0.9 bar and the room temperature is 300 K, then ml/min values are typically found to be roughly 20 % higher than that of sccm readings. For instance, if the flow rate of an MFC is set to 500 sccm, then Agilent ADM 2000 would indicate a total flow rate of 600 ml/min under the aforementioned room temperature and pressure.

Each MFC was also subjected to flow check tests before the experiments. To conduct such a flow check test, V6 was turned off and V5 was turned on to direct the gas flow through Agilent ADM 2000 universal flowmeter (not seen in **Scheme 2-9**) located end of the flow check line (flow check line is highlighted with green arrows in **Scheme 2-9**). **Scheme 2-9** indicates the gas flow direction with white arrows, the green arrows indicate the gas flow direction used in the flow check tests and light blue arrows show the dilution gas (N<sub>2</sub>(g)) pipeline.

#### 2.1.4. SRS RGA-200 Mass Spectrometer and Sampling System

The mass spectrometer which was used as residual gas analyzer in the flow reactor system consists of a quadrupole probe and an electronic control unit (**Scheme 2-10a**). The quadrupole probe has three main subcomponents: the ionizer, the quadrupole filter, and the ion detector (**Scheme 2-10b**). All those parts are operated under high vacuum conditions (*i.e.*,  $10^{-5}$  Torr or less). The ionizer is the first stage of the detection (**Scheme 2-10c**).

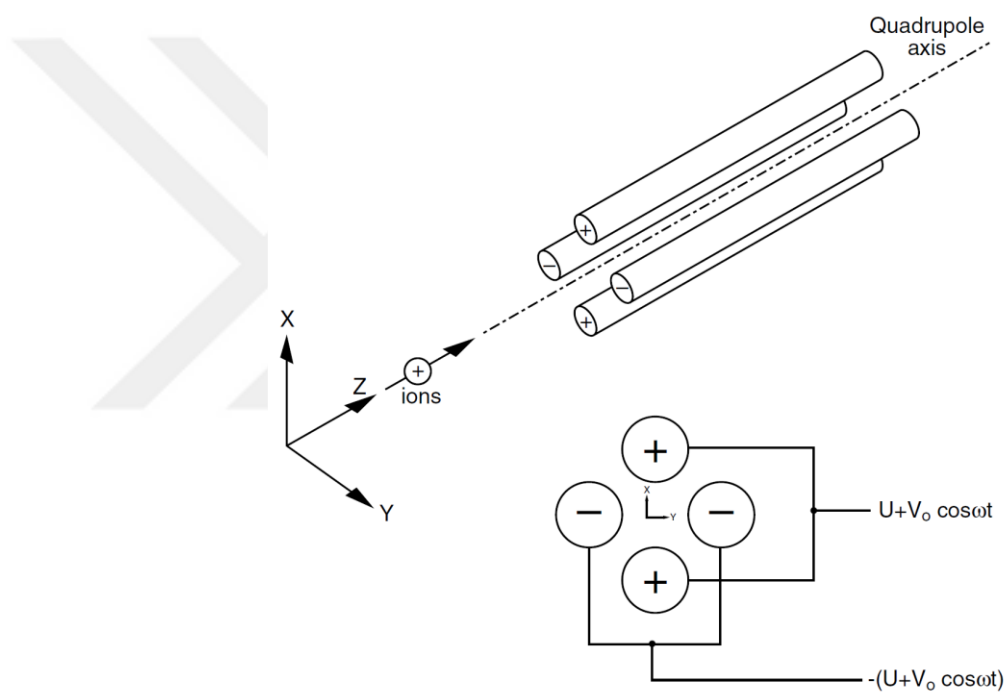


**Scheme 2-10.** SRS RGA-200 mass spectrometer a) quadrupole probe and electronic control unit (ECU), b) subcomponents of the quadrupole, and c) ionizer components. Adapted from Ref [177].

The operation principle of the ionizer is rather similar to a Bayard-Alpert type ionization gauge [177] where a filament ( $\text{ThO}_2$  coated Ir wire) is used as the electron source. The emitted electrons from the filament are accelerated towards anode grid while the negative bias applied on the repeller also prevents escape of the electrons from the ionizer and forces them towards the anode. Before reaching the anode grid, electrons emitted from the hot filament collide with the neutral gas molecules and create positive ions. Ions formed inside the anode grid are directed towards the focus plate with the help of a proper electric field. The net potential on the focus plate is negative with respect to the ground attracting the ionized (cationic) gas particles from the anode grid [177].

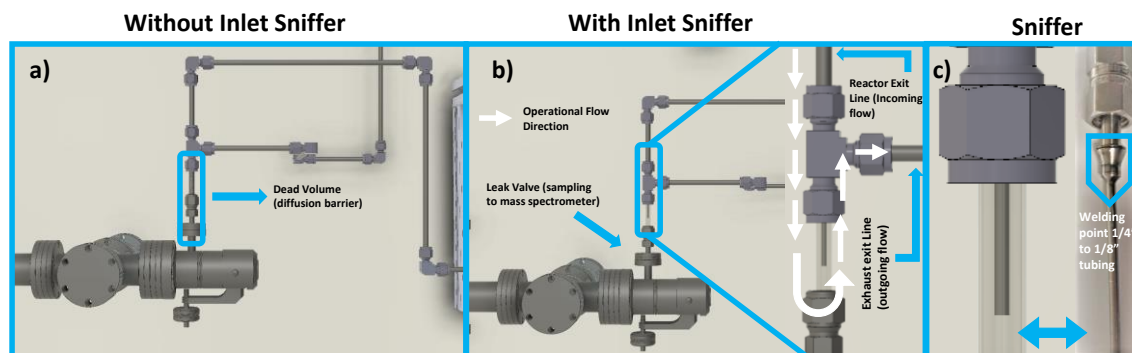
To filter the incoming cations based on their mass to charge ratio ( $m/z$ ) a two-dimensional quadrupole field is created between four electrodes (**Scheme 2-11**). The positively charged ions enter the quadrupole along with the Z-direction and start to oscillate based on their  $m/z$  ratio until reaching the ion detector (*i.e.*, the Faraday cup). The ions are filtered in the

quadrupole, by applying a specific DC offset voltage and an oscillating RF scanning voltage, eliminating the rest of the ions other than ions of interest. Finally, positive ions enter the Faraday cup, impinge on a metal wall and drain electrons from the metal wall which in turn, creates an ion current proportional to the number of incoming positively charged ions. As it was mentioned earlier, mass spectrometers are operational under high vacuum conditions. It means that sample gas cannot be directly fed to the QMS and a special gas sampling capability is required to reduce the atmospheric pressure of the sample gas to low-pressure (*i.e.*, high vacuum) conditions.



**Scheme 2-11.** 2D drawing of the quadrupole mass filter [177].

In an attempt to achieve sensitive and short response gas sensing capabilities, a custom design QMS gas sampler unit was designed and constructed. Location of the QMS gas sampler is designated with a “U” shaped arrow in **Scheme 2-9**. Inefficient feeding of the gas sample to the QMS due to the diffusion limitations was one of the earliest challenges tackled in the initial operational stages of the flow reactor setup. This problem was overcome upon installation of the “sniffer” or gas-sampling unit before the QMS.



**Scheme 2-12.** Description of the sniffer designed for efficient gas sampling to the mass spectrometer.

In the earlier gas sampling designs used in the flow reactor system, extremely long response time (*e.g.*, up to 120-180 s delayed QMS response after switching to a different gas feed) of the QMS was a significant problem. The main reason for the delay in QMS response was the dead volume inside the mass spectrometer inlet gas line before the high precision leak valve (**Scheme 2-12a**). Therefore, between exhaust line of the gas stream and leak valve undesired dead volume established due to design requirements (see **Scheme 2-12a**). Hence, to overcome the diffusion barrier due to the dead volume, a sniffer was designed and constructed (**Schemes 2-12b-12c**). In this design,  $\frac{1}{4}$ " standard gas line coming from the reactor is welded to a  $\frac{1}{8}$ " tubing at the end of the conic ferrule (**Scheme 2-12c**). After this critical design improvement, response time of the QMS was successfully reduced to 5-20 s as a function of the gas flow rate used in the experiment. Note that in order to achieve comparable dosing rates, the pressure on the ionization gauge inside the QMS vacuum chamber was set to  $5 \times 10^{-5}$  Torr prior to each experiment using the leak valve.

### 2.1.5. Teledyne T200 NO<sub>x</sub> Analyzer and Gas Sampling System

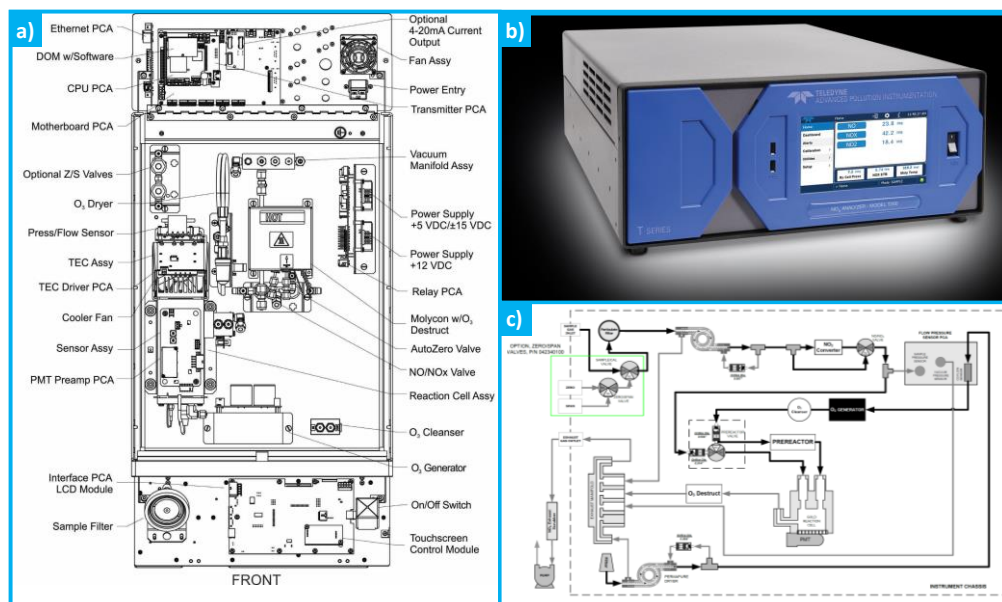
While mass spectroscopy is extremely useful to obtain a real-time identification of the reactants and products emerging from the reactor, there exists various important limitations associated with this detection technique. Since NO<sub>2</sub> is a highly reactive radical, it readily fragments into various components in the QMS ionization chamber where the extent of this fragmentation strongly depends on the experimental condition of the ionizer performance (*e.g.*, aging/surface composition/resistance/thickness/geometric deformations of the ionizer filament). Thus, identification of the true quantities of NO<sub>2</sub> ( $m/z = 46$ ) and its major fragmentation product NO ( $m/z = 30$ ) is a well-known challenge in affordable

QMS systems with low resolving power such as the one used in the current work. Thus, in order to circumvent these limitations, in addition to the QMS, we incorporated a second type of analyzer (Teledyne T200 Chemiluminescence NO<sub>x</sub> Analyzer) to the downstream of the catalytic flow reactor.

Operational principle of the NO<sub>x</sub> analyzer is summarized in **Schemes 2-13a-13c**. First, NO in the gas stream is exposed to O<sub>3</sub> (ozone) yielding excited NO<sub>2</sub> species (*i.e.*, NO<sub>2</sub><sup>\*</sup>) and O<sub>2</sub> as shown in reaction (2-1).



Excited NO<sub>2</sub><sup>\*</sup> species relax to the ground state by emitting photons with particular wavelengths (reaction (2-2)). Emitted photons have a variety of wavelengths ranging within 600 to 3000 nm with an emission maximum at 1200 nm. These emitted photons are detected with the help of a photo multiplier tube (PMT) where the generated signal is directly proportional to the NO<sub>2</sub><sup>\*</sup> amount which is ultimately dictated by the NO concentration in the original sample gas mixture. Thus, this efficient detection scheme can accurately measure NO(g) concentrations within 0.001 ppm to 20 ppm with a 1 Hz (*i.e.*, 1 s<sup>-1</sup>) measurement rate.



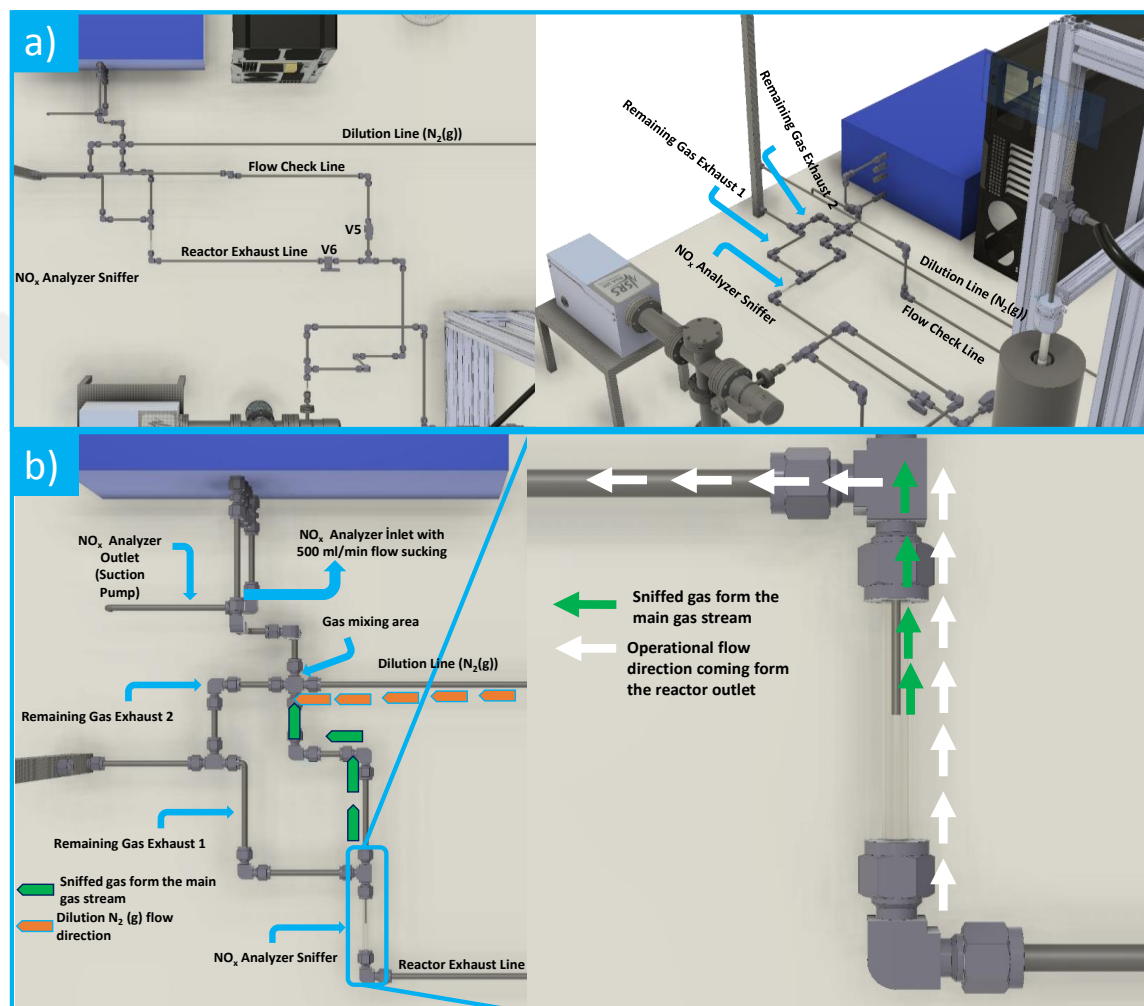
**Scheme 2-13.** Design of the Teledyne T200 NO<sub>x</sub> analyzer a) component based internal design, b) casing of the analyzer, c) pneumatic connections. Adapted from Ref [178].

To determine NO<sub>2</sub> and Total NO<sub>x</sub> (defined as NO<sub>2</sub> + NO) concentrations in the sample gas mixture, a slightly modified detection scheme is utilized. With the help of molybdenum-based NO<sub>2</sub> reduction catalyst operated at 588 K (**Scheme 2-14**), NO<sub>2</sub> present in the sample gas mixture is first reduced to NO (reaction (2-3)). Then, the resultant NO produced from NO<sub>2</sub> reduction is measured in the same way described earlier. To distinguish between NO in the gas stream and the NO from NO<sub>2</sub> reduction, a sequential measurement strategy is applied with the help of pneumatic valves. A certain amount of the incoming gas sample bypasses the NO<sub>2</sub> converter and then rest of it passes through the NO<sub>2</sub> converter. Then, NO from the sample, gas mixture and NO generated from NO<sub>2</sub> reduction are exposed to O<sub>3</sub> at different times to determine NO and NO<sub>2</sub> amounts separately. Once NO and NO<sub>2</sub> concentrations are individually determined, Total NO<sub>x</sub> (NO + NO<sub>2</sub>) in the sample gas mixture can be readily calculated through the summation of these two different measured concentrations. Note that Chemiluminescent NO<sub>x</sub> analyzers are only capable of NO and NO<sub>2</sub> detection and cannot detect other gases such as N<sub>2</sub>O, NO<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>, *etc.*



On the other hand, gas sampling for the NO<sub>x</sub> analyzer in the catalytic flow reactor system also requires a custom-design gas feed scheme. Teledyne T200 NO<sub>x</sub> analyzer is only capable of measuring up to a maximum NO/NO<sub>x</sub> concentration of 20 ppm [178]. However, when the automotive aftertreatment systems are considered, the NO concentration levels are on the order of hundreds of ppm. Therefore, it was necessary to dilute to the gas sample from the reactor outlet (**Scheme 2-14b**). Conventional sample injection strategies involving a pump or an MFC were not adequate options for controlled dilution from the main gas stream. Therefore, the sniffer approach used in the mass spectrometer sampling (**Scheme 2-12b**) was also used in the NO<sub>x</sub> analyzer dilution gas setup. The main difference in these two sniffers is the gas flow direction. While in the mass spectrometer gas sampling, the gas stream was coming out of the sniffer, in the case of the NO<sub>x</sub> analyzer dilution setup, (**Scheme 2-14b**), the gas stream coming from the reactor outlet entered the sniffer. A secondary problem associated with NO<sub>x</sub> analyzer dilution was regarding the precise controlling of the amount of gas that entered the sniffer where the remaining gas stream was directed to gas exhaust 1 (**Scheme 2-14b**). It was noticed that the amount of gas passing

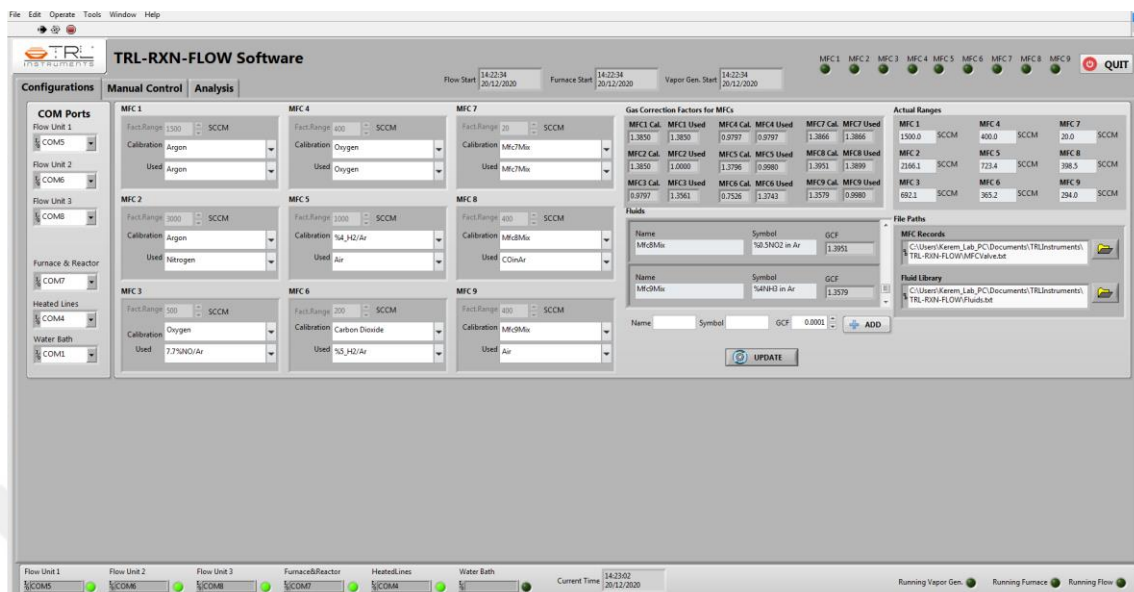
through the sniffer could be controlled by the flow rate of the dilution gas. Hence, different flow rates were tested to successfully dilute the gas sample to a concentration lower than the detection upper limit of the  $\text{NO}_x$  analyzer.



**Scheme 2-14.** The gas pipeline connections from reactor exhaust to the Teledyne T200  $\text{NO}_x$  analyzer; a) distant view for pipeline connections between the analyzer and reactor exhaust b) detailed configuration view for gas sampling from reactor exhaust to the  $\text{NO}_x$  analyzer.

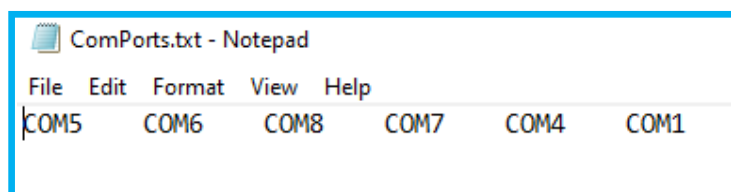
## 2.1.6. LabVIEW Based Flow Reactor Software

The experimental control unit and LabView software were designed together with TerraLab Company (Ankara, Turkey) based on the current experimental demands and operational feedback. In this section, the user interface of the program and experimental method creation are explained in detail. The name of the flow control software is TRL-RXN-FLOW.



**Scheme 2-15.** The configuration tab of the TRL-RXN-FLOW software.

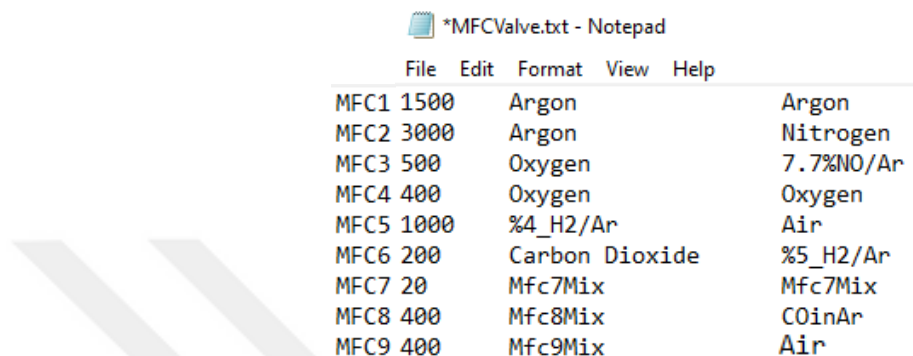
In the earlier sections, it was mentioned that there are 9 MFC located in three different electronic units. Hence, MFCs for each unit, reactor heating system and heating for gas lines (a water bath is designed for humidifying the gas mixture was not used in the current work) must be connected to the computer by choosing appropriate com ports (**Scheme 2-15**). The appropriate com ports can be determined by unplugging specific serial connections from the computer while device manager screen in the windows is monitored. After determination of the corresponding com ports for each flow unit and others, the ComPorts.txt file (**Scheme 2-16**, C:\Users\Administrator\Documents\TRLInstruments\TRL-RXN-FLOW\ComPorts.txt) should be updated to connect experimental control unit with the software.



**Scheme 2-16.** The connection parameters in between computer and TRL-RXN-FLOW software.

The order of the COM numbers in **Scheme 2-16**, start from Flow Unit 1 and follow others from left to right. Same COM numbers are also given top to bottom in **Scheme 2-15**.

In **Scheme 2-15**, configuration tab demonstrates MFC operations (used gas, gas calibration gas, flow range *etc.*), GCF entry tab, and library files for MFC default (see **Scheme 2-17**) values that contain flow rate range with calibration gas and GCFs of different gases and their mixtures.



| File      | Edit | Format                | View | Help                   |
|-----------|------|-----------------------|------|------------------------|
| MFC1 1500 |      | Argon                 |      | Argon                  |
| MFC2 3000 |      | Argon                 |      | Nitrogen               |
| MFC3 500  |      | Oxygen                |      | 7.7%N <sub>2</sub> /Ar |
| MFC4 400  |      | Oxygen                |      | Oxygen                 |
| MFC5 1000 |      | %4_H <sub>2</sub> /Ar |      | Air                    |
| MFC6 200  |      | Carbon Dioxide        |      | %5_H <sub>2</sub> /Ar  |
| MFC7 20   |      | Mfc7Mix               |      | Mfc7Mix                |
| MFC8 400  |      | Mfc8Mix               |      | COinAr                 |
| MFC9 400  |      | Mfc9Mix               |      | Air                    |

**Scheme 2-17.** MFC parameters in TRL-RXN-FLOW software.

In **Scheme 2-15**, the 9 MFCs were given with their properties. There is a term Fact Range (sccm) located below each MFC number in **Scheme 2-15** and in the same location, calibration gas and used gas for the corresponding MFC is also shown. The Fact Range and calibration gas are the factory settings of the corresponding MFC which is specifically written on the calibration sticker of each MFC (**Scheme 2-7**). The Fact Range of the corresponding MFC cannot be modified on the software interface. To modify Fact Ranges MFCValve.txt file should be modified. Then by clicking update button (**Scheme 2-15**) Fact Ranges can be updated (if the change is not visible, software needs to be restarted). Additionally, by clicking the update button in the user interface, calibration and used gas columns in MFCValve.txt file can be updated (**Scheme 2-17**). The first column after Fact Range is the calibration gas and the later gas is the used gas (**Scheme 2-15**). It is extremely important to remember that MFCValve file update is only necessary when a new MFC is mounted in the experiment control unit or in case of changes in the MFC locations in the electronics unit. The fluids file is the library of GCF for the defined fluid which is also accessible in the user interface (**Scheme 2-15**) under the section of fluids. However, if there is a need to use an unregistered gas type in the Fluids.txt file, the new GCF can be added by filling Name, Symbol and GCF box in the user interface (**Scheme 2-15**). The GCF of single specimen or mixtures can be calculated by using the excel file demonstrated in **Table 2-2** and it can be inserted into the fluid library by using configuration tab in **Scheme 2-15**.

Then added gas can be selected for the corresponding MFC from dropdown menu (**Scheme 2-15**). As can be seen in the configuration tab of the software (**Scheme 2-15**), there are boxes labeled as Gas Correction Factors for MFCs and Actual Ranges to explore the currently used MFC parameters. For instance, in **Scheme 2-15**, for MFC2 calibration gas is Ar(g) and Fact Range for Ar(g) is 3000 sccm, but the actually used gas in MFC2 is N<sub>2</sub> (g). The Gas Correction Factor for MFCs and Actual Ranges sections in the configuration tab show the calibration gas GCF, used gas GCF and the maximum range flow for the used gas. Hence, those sections were designed to see updated GCFs results when a gas is used other than calibration gas. Therefore, this custom-design user interface allows us to add/remove any type of MFCs and gases that open playground for customized experiments.

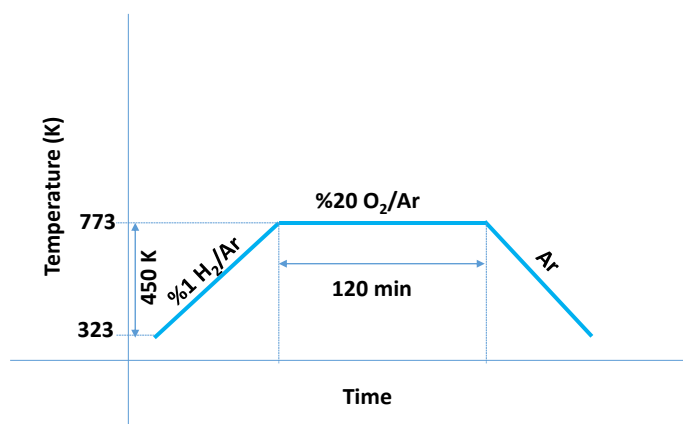


**Scheme 2-18.** The analysis tab of the TRL-RXN-FLOW software.

Analysis tab demonstrated in **Scheme 2-18** shows the experimental method parameters as a function of time including temperature and flow rates of the MFCs. The “clear graphs” function (**Scheme 2-18**) is used to remove remaining data from the previous experiments. It can also be used to start the data recording at the same time with other devices/instruments such as mass spectrometer or NO<sub>x</sub> analyzer in a synchronous manner which allows the use of the same time domain for different data sets acquired by different instruments. The “log furnace” function (**Scheme 2-18**) is another crucial function that regulates log time for data acquisition. Time control for data logging is significantly important to record equal number of data points in the same time domain. Although, there

is a log time control in the software, SRS RGA 200 QMS software program does not provide data acquisition at equal time intervals. Due to different numbers of data points collected by the mass spectrometer and the flow reactor software, it is not possible to match and analyze them directly. Therefore, to equalize the number data points coming from the mass spectrometer and flow reactor software and synchronize these data points in the same time domain, an external software can be used (*e.g.*, “interpolation function” of Origin Pro 2016 or later versions of this software).

The creation and registration of the experimental method is necessary to conduct accurate and automated experiments. As it was mentioned before, the method files created in the form of txt can be transferred to the Analysis tab user interface (**Scheme 2-18**, Flow Profile and Temperature Profile sections).



**Scheme 2-19.** Illustration of simple multi-step experiment designed for the flow reactor system.

To provide further insights about experimental method creation, the example experiment presented in **Scheme 2-19** is chosen. In the example experimental method, total gas flow rate is set to 1000 sccm. The reactor is heated from 323 to 773 K with a 5 K/min heating rate in the presence of 1% H<sub>2</sub>/Ar. Then, at 773 K, gas feed is switched to 20 % O<sub>2</sub>/Ar for 120 min and finally, reactor is cooled down to 323 K with 5 K/min cooling rate in the presence of Ar (purge gas) flow.

The Flow Profile and Temperature Profile txt files are demonstrated in **Scheme 2-20**. As can be seen in **Scheme 2-18**, in Flow Profile section, there are various step numbers for MFCs. The step number is used to define flow rates of different MFCs (**Scheme 2-20**). If we consider the example experiment given in **Scheme 2-19**, there are three different steps

which include heating with 1% H<sub>2</sub>/Ar, soaking with 20% O<sub>2</sub>/Ar and cooling with Ar. Thus, MFC1 (Pure Ar), MFC4 (Pure O<sub>2</sub>) and MFC6 (5% H<sub>2</sub>/Ar) can be used to design such an example experiment (**Scheme 2-17**).

| a) MFCs Flow Method                |      |        |      |      | b) Temperature Method               |      |        |      |      |
|------------------------------------|------|--------|------|------|-------------------------------------|------|--------|------|------|
| *Example_Method_for_MFC_Flow.txt - |      |        |      |      | *Example_Method_for_Temperature.txt |      |        |      |      |
| File                               | Edit | Format | View | Help | File                                | Edit | Format | View | Help |
| MFC1                               | 1    | 800    | 90   |      | 0                                   | 5    | 773    |      |      |
| MFC1                               | 2    | 800    | 120  |      | 120                                 | 0    | 773    |      |      |
| MFC1                               | 3    | 1000   | 90   |      | 0                                   | 5    | 323    |      |      |
| MFC4                               | 1    | 0      | 90   |      |                                     |      |        |      |      |
| MFC4                               | 2    | 200    | 120  |      |                                     |      |        |      |      |
| MFC4                               | 3    | 0      | 90   |      |                                     |      |        |      |      |
| MFC6                               | 1    | 200    | 90   |      |                                     |      |        |      |      |
| MFC6                               | 2    | 0      | 120  |      |                                     |      |        |      |      |
| MFC6                               | 3    | 0      | 90   |      |                                     |      |        |      |      |

**Scheme 2-20.** Example method txt files a) Flow profile and b) Temperature profile.

To obtain a 1% H<sub>2</sub>/Ar gas feed, 5% H<sub>2</sub>/Ar gas cylinder (i.e., the hydrogen source) should be diluted with Ar(g), where ratio of the MFC6 flow rate to the total flow rate should have 1:5. Hence, if we consider total flow is 1000 sccm, MFC1 should be 800 sccm where MFC6 has 200 sccm flow. The difference between 323 and 773 K is 450 K suggesting that a total ramp time of 90 min is needed to reach 773 K with a 5 K/min heating ramp rate. Additionally, MFC4 flow rate should be “0” sccm during this 90 min as there is no involvement of MFC4 in step 1. Values given in the **Scheme 2-20a** indicate that, firstly corresponding MFCs are flowed by the given step numbers, flow rates (sccm), and flow durations/times (min). For step 2, MFC4 and MFC1 can be used to create a 20% O<sub>2</sub>/Ar (g) mixture. MFC4 provides pure O<sub>2</sub>(g). Hence, to have 20% O<sub>2</sub> in the total flow of 1000 sccm, MFC4 should be set to 200 sccm where MFC1 flow rate should be set to 800 sccm. Furthermore, there is no involvement of MFC6 in step 2, so its flow rate is equal to “0”. As it was indicated in **Scheme 2-19**, the soaking time is 120 min. Thus, step 2-time parameter should be set as 120 min. For step 3, the system is cooled from 773 K to 323 K with a 5 K/min cooling rate suggesting that 90 min duration is enough for this step. The MFC1 flow rate can be set as 1000 sccm, where MFC4 and MFC6 flow rate must be set to “0” sccm for step 3.

The temperature profile method file creation is simpler than the flow profile method file. To prepare temperature profile method file, it is important to determine whether heating, cooling, or soaking of the catalyst is needed. In this example experiment, first step is heating from 323 K to 773 K with a 5 K/min heating rate. This step can be written on a single line (**Scheme 2-20b**). The first column in the temperature profile file is the duration which should be always set to “0” for heating or cooling processes which are controlled by the PID controller. Therefore, time for step 1 is set to “0”. The second column shows the cooling/heating rate of the process in terms of K/min. In this case, it is 5 K/min for the step 1. The last column is the target temperature, which is 773 K for step 1. Step 2 is soaking, so first column (*i.e.*, soaking duration) must be 120 min and the ramp rate must be set to “0” for soaking. The target temperature can be written as the soaking temperature which is 773 K for the step 2. The last step of this experiment is cooling. Actually, this step is similar to step 1. The only difference is the target temperature which should be entered as 323 K for cooling step (the software uses Celsius units so in real experiments temperature values should be entered as Celsius). One last reminder about the method files can be related to the preparation of those files. Either the method files can be prepared by using the user interface of the flow reactor software or they can be prepared directly via txt files and then imported to the software. Additionally, prepared methods on the flow reactor software can be saved or changed by clicking on the save button (**Scheme 2-18**).

Lastly, to start data recording of the furnace (reactor) temperature, “log furnace” icon must turn into green color and after the end of the experiment; it should turn into grey color. In order to save the temperature and flow data, in the analysis tab, one needs to right click on the corresponding data figure (**Scheme 2-18**), upon appearance of the option list, “save data as excel file” or “copy to clipboard” (copy to empty text file) option can be chosen.

During the routine operation of the flow reactor system, the manual control interface can be used to design trial flows or to troubleshoot/isolate various hardware problems. In the manual control tab, heated lines (flow reactor inlet, by-pass line and exhaust of the flow reactor can be heated to prevent condensation of water or to decrease the amount of adsorbed water on the walls) and furnace temperature can be controlled manually. Flow rate of each MFC can be set by entering the desired value into the Target (sccm) box

(**Scheme 2-21**). The volt values are displayed in “Set (volts)” box based on the entered flow rates. The feedback signals from the corresponding MFCs versus entered flow rates are also displayed in “Actual (volts)” box. These voltage readings are essential for the isolation of the hardware problems associated with the flow rates and determination of the flow resolution of the corresponding MFC. At the initial versions of flow reactor setup and software, the desired flow rates could not be accurately controlled due to hardware problems associated with MFCs and electronic cards and isolation of such problems was time consuming. Therefore, in an attempt to quickly isolate the hardware problems, “set volts” and feedback “actual volts” and their communication electronics (see **Scheme 2-21**, Err Adam1, Err BQ1 *etc.*) are constantly monitored during the experiment. Furthermore, the flow rate resolution can also be found out for each MFC by determining the lowest voltage applicable in the manual control tab. As mentioned earlier, MFC flow range is controlled with a 0 to 5 VDC analog signal. The lowest voltage step for this electronic design is 0.01 in 0 to 5 VDC range. Therefore, flow rate resolution (*i.e.*, minimum flow rate available) can be calculated for a corresponding MFC by dividing the maximum flow rate of the MFC by 500. Additionally, there could be a voltage offset between set volts and the actual volts (feedback signal) which is typically in the level of 0.02 V. Therefore, this difference should be identified for each MFC and added to the desired flow value. For instance, to reach a 500 sccm flow rate with a 0.02 V offset for MFC1, 506 sccm flow rate should be entered.



**Scheme 2-21.** The manual control tab of the TRL-RXN-FLOW software.

## CHAPTER 3

### 3. Material Synthesis and Instrumentation

#### 3.1. Perovskite ( $\text{La}_x\text{Co}_y\text{Mn}_z\text{O}_{3+a}$ ) Synthesis as a DOC Catalyst

All metal precursors and chemicals,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), were purchased from Sigma Aldrich with purity of  $\geq 99.5\%$ ,  $\geq 97\%$ ,  $\geq 98\%$  and  $\geq 99.5\%$ , respectively. The citrate method, developed by General Motors Company, was used to synthesize  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  benchmark perovskites [179], while a slightly modified version of this protocol was utilized for the synthesis of  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  (B-site mixed) perovskites. For the synthesis of a 3 g perovskite sample batch, citric acid was dissolved in deionized water and appropriate amounts of metal precursors (**Table 3-1**) were added to the acidic medium. The solution was stirred for 1 h under ambient conditions and then heated at 353 K with constant stirring until the gel formation was obtained. After the formation of the gel, samples were dried at 363 K under ambient conditions for 24 h. Dried samples were pulverized to obtain a fine powder. Finally, powder samples were calcined at 973 K in air for 5 h. In the synthesis of  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  B-site mixed perovskites, Co and Mn precursors were added to the solution simultaneously. The concentrations of the metal precursors were altered to adjust the “x” values in the  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  B-site mixed perovskites within  $0.1 \leq x \leq 0.9$ .

**Table 3-1.** The precursor amounts for synthesized perovskites.

| $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$ | $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O/g}$ | $\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O/g}$ | $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O/g}$ | Citric Acid/g | Distilled Water/ml | Calc. Temp/K |
|------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|---------------|--------------------|--------------|
| x=0                                      | 1.791                                                  | 1.038                                                  | ---                                                    | 1.912         | 82.7               | 973          |
| x=0.1                                    | 1.788                                                  | 0.933                                                  | 0.120                                                  | 1.909         | 82.6               | 973          |
| x=0.2                                    | 1.785                                                  | 0.828                                                  | 0.240                                                  | 1.902         | 82.4               | 973          |
| x=0.3                                    | 1.782                                                  | 0.723                                                  | 0.359                                                  | 1.902         | 82.2               | 973          |
| x=0.4                                    | 1.779                                                  | 0.619                                                  | 0.478                                                  | 1.899         | 82.2               | 973          |
| x=0.5                                    | 1.776                                                  | 0.515                                                  | 0.597                                                  | 1.896         | 82.0               | 973          |
| x=0.6                                    | 1.773                                                  | 0.411                                                  | 0.715                                                  | 1.893         | 82.0               | 973          |
| x=0.7                                    | 1.770                                                  | 0.308                                                  | 0.833                                                  | 1.890         | 81.8               | 973          |
| x=0.8                                    | 1.767                                                  | 0.205                                                  | 0.950                                                  | 1.887         | 81.6               | 973          |
| x=0.9                                    | 1.764                                                  | 0.102                                                  | 1.067                                                  | 1.883         | 81.5               | 973          |
| x=1.0                                    | 1.761                                                  | ---                                                    | 1.184                                                  | 1.881         | 81.3               | 973          |

### 3.2. Synthesis of Fe and/or Co Based SCR Catalysts

In the synthesis of Fe and Co based SCR catalysts, various supports from the Daiichi Kigenso Kagaku Kogyo Company (DKKK, Osaka, Japan) [180] were used to investigate the support effect on NO reduction activity. Utilized amounts Fe and/or Co precursors ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  Sigma Aldrich  $\geq 98\%$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  Sigma Aldrich  $\geq 98\%$ ) and supports for the synthesis of SCR catalysts are given in **Table 3-2**. Calculated masses of the corresponding support material for each catalyst in **Table 3-2** were transferred to different beakers. Then deionized water is added to each beaker by arranging the final volume of the solution as 40 ml. The solution is stirred for 60 min at 500 rpm. Necessary masses of the active metal precursors of Fe and/or Co for a given metal loading were added to the solution, while solution was being stirred. The solution volume was adjusted to 60 ml by adding deionized water followed by stirring for 60 min at 353 K. The temperature was measured with the thermocouple positioned in the solution. Then, the solution was dried at 393 K for 18 h. Dried samples were calcined in air at 823 K for 3 h, where the heating rate was set to 2 K/min.

**Table 3-2.** The precursor amounts for synthesized Fe and/or Co based SCR catalysts.

| Metal Loading wt % | Fe (Metal Basis)/ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /mg | Co (Metal Basis)/ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /mg | Support/Mass/mg                                   | Calc. Temp./K |
|--------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------|---------------|
| 1% Fe              | 20/146                                                                     | ---                                                                        | $\text{CeO}_2$ /1980                              | 823           |
| 2% Fe              | 40/292                                                                     | ---                                                                        | $\text{CeO}_2$ /1960                              | 823           |
| 4% Fe              | 80/584                                                                     | ---                                                                        | $\text{CeO}_2$ /1920                              | 823           |
| 6% Fe              | 120/876                                                                    | ---                                                                        | $\text{CeO}_2$ /1880                              | 823           |
| 8% Fe              | 160/1168                                                                   | ---                                                                        | $\text{CeO}_2$ /1840                              | 823           |
| 20% Fe             | 400/2920                                                                   | ---                                                                        | $\text{CeO}_2$ /1600                              | 823           |
| 4% Fe              | 80/584                                                                     | ---                                                                        | $\text{CeO}_2$ -Type B/1920                       | 823           |
| 2% Co              | ---                                                                        | 40/198                                                                     | $\text{CeO}_2$ /1960                              | 823           |
| 4% Co              | ---                                                                        | 80/396                                                                     | $\text{CeO}_2$ /1920                              | 823           |
| 6% Co              | ---                                                                        | 160/792                                                                    | $\text{CeO}_2$ /1840                              | 823           |
| 4% Fe-4% Co        | 80/584                                                                     | 80/396                                                                     | $\text{CeO}_2$ /1840                              | 823           |
| 4% Fe-4% Co        | 80/584                                                                     | 80/396                                                                     | 10% $\text{WO}_3$ - $\text{ZrO}_2$ /1840          | 823           |
| 4% Fe-4% Co        | 80/584                                                                     | 80/396                                                                     | 9% $\text{La}_2\text{O}_3$ - $\text{ZrO}_2$ /1840 | 823           |
| 4% Fe-4% Co        | 80/584                                                                     | 80/396                                                                     | 50% $\text{CeO}_2$ - $\text{ZrO}_2$ /1840         | 823           |

### 3.3. Synthesis of Benchmark 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> PGM Catalyst

1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark PGM catalyst was synthesized to compare the catalytic activities of perovskite-based DOC catalysts and Fe and/or Co based SCR catalyst with a precious metal benchmark catalyst. Incipient to wetness impregnation (IWI) method was used to synthesize 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>. 990 mg of support material (Alfa Aesar, aluminum oxide, gamma phase, 3.2 mm tablets, 175 m<sup>2</sup>/g  $\geq 96$  %) is placed into the two-neck-Erlenmeyer flask where vertical neck was connected to a vacuum pump and the horizontal one was coupled to a peristaltic pump. Before the peristaltic pump was turned on, precursor solution injection (flow) rate was set to 0.1 ml/min. The sealed Erlenmeyer flask was placed in a sonicator for homogeneous distribution of Pt precursor on the alumina support. Before the precursor solution injection, support material was outgassed under vacuum for 30 min at 20 kPa in order to evacuate the pores of the alumina support material for better Pt uptake. 480  $\mu$ l (10 mg, Pt metal basis) of the precursor solution (Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>), Sigma-Aldrich diamine dinitritoplatinum(II), 3.4 wt. % solution in dilute NH<sub>3</sub>(aq)) which was dissolved in 1.5 ml deionized water was impregnated onto the support by using IWI setup as described above. After the completion of impregnation, Erlenmeyer flask was kept in vacuum for 40 min at 400 mmHg for drying. The slurry from the IWI was collected in a container and dried at 353 K for 3 h. The dried samples were calcined in air at 823 K for 3 h where the heating rate was set to 2 K/min.

### 3.4. XRD

A Rigaku X-ray diffractometer, equipped with a miniflex goniometer and Cu-K $\alpha$  X-ray source with 1.5418 Å wavelength, 30 kV energy and 15 mA current, was utilized to collect XRD data where 0.02° s<sup>-1</sup> step resolution was chosen within 10-80° as 2 $\theta$  operational angle. For SCR catalysts, XRD patterns of the samples were obtained by using a Panalytical Multi-Purpose X-Ray diffractometer equipped with a Cu K $\alpha$  (1.5405 Å) X-Ray source operating at 45 kV/40 mA where the scan rate was set to 0.01° s<sup>-1</sup>. The assigned crystal structures were determined via ICDD (International Centre for Diffraction Database) crystal structure library.

### 3.5. XPS

XPS measurements were carried out via a SPECS XP spectrometer with a PHOIBOS MCD-9 hemispherical energy analyzer and a mono-chromatic Al K $\alpha$  X-ray irradiation ( $h\nu$  = 1486.6 eV, 350 W). The powder samples were positioned on sticky a copper tape. An electron flood gun (SPECS FG-15/40, 3.0 eV, 70  $\mu$ A) were used in the XPS measurements for charge compensation. For perovskite samples, due to the complexity of the C 1s signal, XPS binding energy (B.E.) positions were calibrated using the La 3d $_{5/2}$  signal at 834.7 eV corresponding to the La<sup>3+</sup> states.

### 3.6. N<sub>2</sub> Adsorption-Desorption Measurements

A Micromeritics Tristar3000 surface area and pore size analyzer apparatus was used to determine the specific surface area (SSA) values of the catalysts by using 5-point low temperature isothermal adsorption, desorption curves of N<sub>2</sub>, and BET method

### 3.7. TEM Measurements

Transmission electron microscopy (TEM) imaging experiments were conducted on a FEI tecnai G2 F30 electron microscope with a 0.17 nm point resolution which is equipped with a Gatan slow-scan CCD camera and a Gatan serial energy loss spectrometer. An electron beam energy of 300 keV was used in the TEM imaging experiments.

### 3.8. ICP-MS Measurements

Elemental compositions of the synthesized B-site mixed perovskites were investigated using an Agilent 7700x Inductively Coupled Plasma Mass spectrometer (ICP-MS). Prior to ICP-MS measurements, calibration curves were prepared for each investigated metal via reference solutions. Each perovskite catalyst was dissolved in 2 % w/w HNO<sub>3</sub> (aq) and sonicated for 10 min. Nominal concentration of each sample solution was set to 5 ppm (metal-basis). For the ICP-MS analysis of each catalyst (*i.e.*, for each perovskite), two different samples were taken, and each sample was measured 5 times. Standard deviations in ICP-MS measurements from the mean values were typically smaller than 1 %.

### 3.9. ATR-FTIR Measurements

Bruker Alpha Platinum FTIR spectrometer were used for Attenuated Total Reflectance Infrared (ATR-FTIR) experiments. A diamond ATR crystal equipped with a Deuterated Triglycine Sulfate (DTGS) IR detector (temperature-dependent ferrocrystals of DTGS) operating in Mid-IR frequency region ( $400\text{--}4000\text{ cm}^{-1}$ ) were employed. ATR-FTIR spectra were acquired with a  $2\text{ cm}^{-1}$  spectral resolution by averaging 64 scans.

### 3.10. Raman Measurements

A Renishaw inVia-Reflex confocal Raman spectrometer was used to analyze SCR catalysts. The Raman spectrometer was equipped with a 532 nm (green) laser and an adjustable power dial with a maximum power of 50 mW. Each Raman spectrum was recorded with  $1\text{ cm}^{-1}$  resolution.

### 3.11. H<sub>2</sub>-TPR Measurements

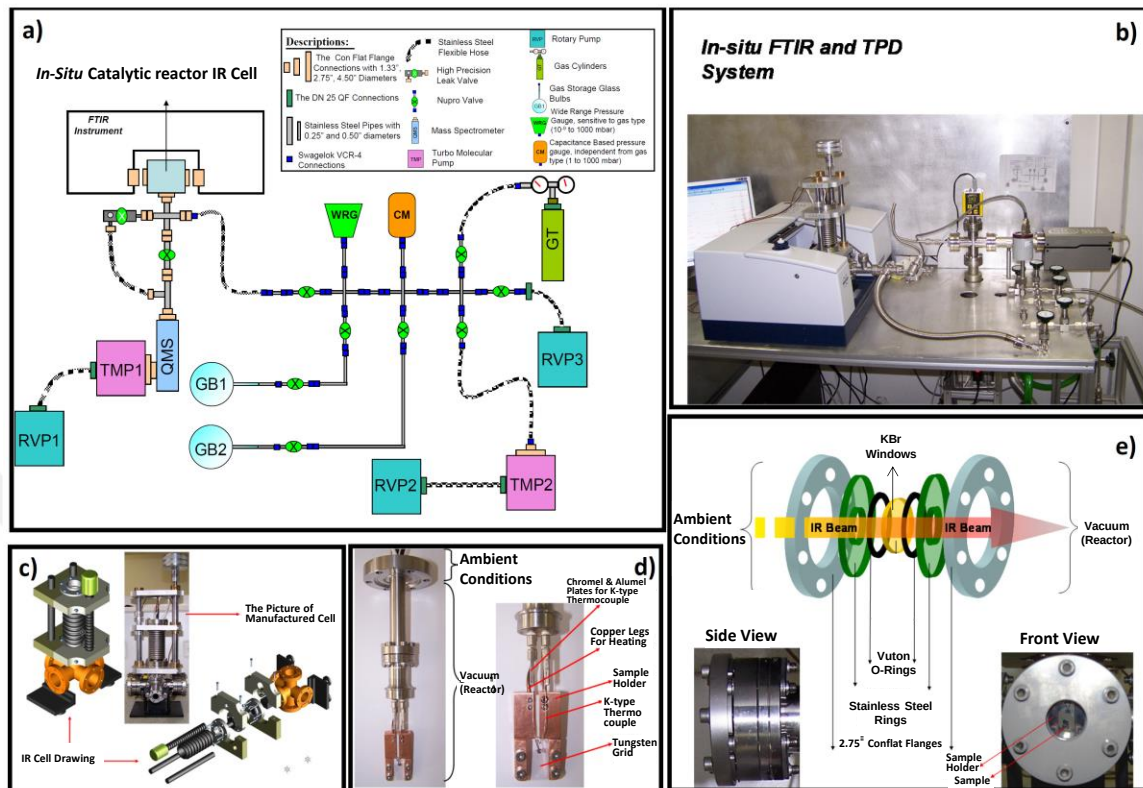
In the H<sub>2</sub>-TPR experiments, 125 mg of a given perovskite sample with a 45-60 mesh size was inserted into the quartz flow reactor. Firstly, each catalyst was pretreated in 4 % H<sub>2</sub>/Ar flow for 1 h at 773 K with a 500 ml (STP) min<sup>-1</sup> total flow rate. Then, the gas feed was switched to pure Ar(g) for 1 h at 773 K with a 500 ml (STP) min<sup>-1</sup> flow rate. The final step of the pretreatment was completed with 20 % O<sub>2</sub>/Ar flow for 1 h at 773 K with a flow rate of 500 ml (STP) min<sup>-1</sup>. Then the catalyst was cooled to 300 K in 20 % O<sub>2</sub>/Ar mixture without changing the flow rate. This pretreatment procedure ensured surface cleaning and removal of adsorbed molecular water from the catalyst surfaces. After the completion of the pretreatment of the perovskite catalysts, gas feed was switched to 4 % H<sub>2</sub>/Ar flow with a 500 ml (STP) min<sup>-1</sup> total flow rate for 4 h in order to stabilize H<sub>2</sub>O (m/z=18) Quadruple Mass Spectrometer (QMS) signal intensity. Once the QMS water signal reached a steady state, catalyst was heated to 1173 K with a heating rate of 6 K.min<sup>-1</sup> in the presence of 4 % H<sub>2</sub>/Ar with a 500 ml (STP) min<sup>-1</sup> flow rate. Reduction process was monitored by recording the Quadruple Mass Spectrometer (QMS) signal intensity of the H<sub>2</sub>O (m/z=18) as a function of temperature.

### 3.12. *In-situ* and *Ex-situ* XANES and *Ex-situ* EXAFS Measurements

All XANES measurements were carried out at the Samba beamline of Soleil Synchrotron facility (Paris, France) operating at 2.75 GeV. XANES experiments were performed for Co-K (7709 eV), Mn-K (6539 eV) and La L-III (5483 eV) edges in transmission and/or fluorescence modes. For each measured sample, at least two subsequent spectra were acquired to enhance the signal to noise ratio (S/N). Data analysis was performed using the ATHENA software [181]. *In-situ* XANES experiments were carried out at various temperatures (323-973 K with a 10 K/min linear ramp rate) in the presence of H<sub>2</sub>(g) (5 % H<sub>2</sub>/He, 50 ml/min) or O<sub>2</sub>(g) (10 % O<sub>2</sub>/He, 50 ml/min) by using an *in-situ* glass capillary tube reactor. The EXAFS measurements were conducted in the P65 beamline of DESY (Deutsches Elektronen Synchrotron, Hamburg, Germany). Two successive spectra were recorded at each edge (*i.e.*, Co-K (7709 eV), Mn-K (6539 eV)) and energy calibration was achieved using Co or Mn metal foils. The experiments were carried in transmission mode equipped with three different ionization chambers (for I<sub>0</sub>, I<sub>Sample</sub>, and I<sub>Reference Foil</sub>). Powder samples were mounted on the sticky surface of the double-sided X-ray transparent Kapton tape. Theoretical calculation of each scattering path was done via FEFF/IFEFFIT code in Demeter software package [181] by using appropriate crystal structure data obtained from the XRD spectra.

### 3.13. *In-situ* Fourier Transform Infrared (FTIR) and Temperature Programmed Desorption Experiments

*In-situ* FTIR experiments were performed in transmission mode by using a batch-type spectroscopic reactor equipped with a Bruker Tensor 27 FTIR spectrometer, and a liquid nitrogen-cooled MCT detector. This *in-situ* FTIR system was also coupled to a quadrupole mass spectrometer (QMS, Stanford Research Systems, RGA 200) for TPD experiments.



**Scheme 3-1.** The custom design in-situ FTIR and TPD system in Ozensoy Research Group: a) main parts and connections of the whole system, b) general view of the IR and TPD system, c) in-situ spectroscopic reactor design, d) sample holder, e) custom design IR windows of the spectroscopic cell.

### 3.14. *In-situ* NO<sub>x</sub> Adsorption and TPD Experiments on Perovskites

Before the *in-situ* FTIR spectroscopy experiments, samples were outgassed in the spectroscopic batch reactor under vacuum ( $< 10^{-3}$  Torr) at 403 K for 12 h to clean/outgas the catalyst surface. In all of the *in-situ* FTIR and TPD experiments, self-supported samples (without KBr dilution) were pressed on a tungsten grid ( $\sim 20$  mg/cm<sup>2</sup>) attached to sample holder and placed into the custom-design transmission-mode *in-situ* FTIR cell. Then, catalyst surfaces were exposed to 0.5 Torr NO<sub>2</sub>(g) for 5 min at 323 K followed by evacuation ( $< 10^{-3}$  Torr) and annealing in vacuum using a linear heating ramp (12 K/min) from 323 K to 973 K for further pretreatment and oxidative cleaning of the surface. NO<sub>2</sub>(g) is prepared by mixing NO(g) and O<sub>2</sub>(g) (NO(g), Air Products, 99.9 % purity and O<sub>2</sub>(g) Linde GmbH, 99.999% purity) gases followed by a freeze-thaw-pump cycles for purification. Next, NO<sub>2</sub> adsorption and desorption experiments were performed by dosing 5.0 Torr NO<sub>2</sub>(g) over the sample for 10 min at 323 K and this step was completed by TPD experiments. For further *in-situ* FTIR and TPD analysis, perovskite surfaces were reduced

in the presence of 5 Torr H<sub>2</sub>(g) (Linde GmbH, Germany, > 99.9 %) at 623 K for 10 min in the spectroscopic batch reactor. These pre-reduced perovskite surfaces were re-exposed to 5.0 Torr NO<sub>2</sub> (g) for 10 min at 323 K for additional adsorption and desorption experiments. All IR spectra were collected at 323 K (all *in-situ* IR experiments used 4 cm<sup>-1</sup> resolution and 128 averaged scan). TPD experiments were performed under vacuum (< 10<sup>-5</sup> Torr) with a heating rate of 12 K/min. Relative NO<sub>x</sub> storage adsorption values derived from the TPD data were calculated by considering the mass spectroscopic fragmentation patterns of all of the N-containing desorption species.

### 3.15. The NO<sub>x</sub> Storage Calculation of Perovskites via TPD Experiments

Total amounts of NO<sub>x</sub> species generated on the perovskites due to catalytic NO<sub>x</sub> oxidation were calculated by utilizing integrated TPD signals and QMS fragmentation patterns of NO<sub>2</sub>, NO, N<sub>2</sub>O and N<sub>2</sub> species. The NO<sub>2</sub>(g) decomposes in the ionization chamber of QMS (SRS RGA 200) with a NO:NO<sub>2</sub> intensity ratio of 3.23:1. Hence, integrated signal of NO<sub>2</sub>, m/z=46 (I46) should be multiplied by a factor of 3.23+1.00 = 4.23 to obtain the actual amount of NO<sub>2</sub> release before fragmentation. This corrected NO<sub>2</sub> amount is denoted as “x”. The N<sub>2</sub>O m/z=44 signal fragments as NO and N<sub>2</sub>O with an intensity ratio of 0.34:1. Therefore integrated signal of N<sub>2</sub>O should be multiplied with 0.34 and this corrected value is denoted by “y”. It is important to note that there are multiple contributions to NO m/z=30 signal based on the fragmentations of N<sub>2</sub>O and NO<sub>2</sub>. Hence, contribution of these species should be subtracted from NO m/z=30 (I30) signal to obtain actual NO desorption from the surface. It was mentioned earlier that the fragmentation of NO<sub>2</sub> leads to signals with the relative intensities of NO: NO<sub>2</sub> is 3.23:1 and the fragmentation of N<sub>2</sub>O leads to signals with the relative intensities of NO: N<sub>2</sub>O is 0.34:1. Therefore, contributions of NO<sub>2</sub> and N<sub>2</sub>O were subtracted from the raw NO signal in order to obtain the actual NO release, which is shown with “z”. The m/z=28 N<sub>2</sub> signal (I28) was also enhanced by the fragmentation of N<sub>2</sub>O with an intensity ratio N<sub>2</sub>: N<sub>2</sub>O, 0.11:1. After the subtraction of this contribution, actual amount of N<sub>2</sub> release can be found which is given as “t”. Therefore, total NO<sub>x</sub> storage on each catalyst after catalytic NO<sub>x</sub> oxidation was obtained using the following calculations:

$$x = \text{Quantity of } NO_2 = \left( \int I_{46} \cdot \Delta T \right) \times 4.23 \quad 3-1$$

$$y = \text{Quantity of } N_2O = (\int I_{144} \cdot \Delta T) \times 1.34 \quad 3-2$$

$$z = \text{Quantity of } NO = (\int I_{130} \cdot \Delta T) - (\int I_{146} \cdot \Delta T) \times 3.23 - (\int I_{144} \cdot \Delta T) \times 0.33 \quad 3-3$$

$$t = \text{Quantity of } N_2 = [(\int I_{128} \cdot \Delta T) - (\int I_{144} \cdot \Delta T) \times 0.11] \quad 3-4$$

$$\Sigma \text{Total } NO_x \text{ Adsorption} = x + 2y + z + 2t \quad 3-5$$

### 3.16. Oxygen Vacancy Demonstration on LaMnO<sub>3</sub> with O<sub>2</sub> Adsorption at Low Temperature

*This section is reprinted (adapted) with permission of (Y. Sahin, A. T. Sika-Nartey, K. E. Ercan, Y. Koçak, S. Şenol, E. Ozensoy, Y. E. Türkmen "Precious Metal-Free LaMnO<sub>3</sub> Perovskite Catalyst with an Optimized Nanostructure for Aerobic C-H Bond Activation Reactions: Alkylarene Oxidation and Naphthol Dimerization," ACS Applied Materials & Interfaces, 2021 (13) 5099-5110). Copyright (2022) American Chemical Society.*

Low temperature O<sub>2</sub>(g) adsorption experiments on LaMnO<sub>3</sub> were performed by using an *In-situ* infrared (FTIR) spectroscopic cell (see **section 3.13**) with liquid N<sub>2</sub>. About 25 mg of finely ground LaMnO<sub>3</sub> was pressed onto a high transmittance, lithographically etched fine-tungsten grid, which was mounted on a copper sample holder assembly. Prior to data acquisition, the *in-situ* reactor chamber was evacuated to  $5 \times 10^{-6}$  Torr. Next, 5 Torr 5% H<sub>2</sub>/Ar was dosed over the sample at room temperature (RT), then heated to 673 K, and held for 10 min in the presence of the H<sub>2</sub>/Ar gas mixture. After the reduction protocol, the sample was cooled to RT, where the gas mixture was evacuated to  $5 \times 10^{-6}$  Torr. At this stage, the sample was cooled to 142 K by recirculating liquid nitrogen around the sample holder. After having taken a background FTIR spectrum at 142 K in vacuum, 1 Torr O<sub>2</sub> was dosed over the sample for 1 min followed by subsequent evacuation for 1 min and sample spectrum acquisition. After the sample spectrum acquisition, the sample was brought back to RT. Then, by utilizing the same background spectrum, the steps described above were repeated by altering the reduction temperature to 773, 873, 973, and 1073 K. *In-situ* FTIR spectra were recorded with a resolution of 2 cm<sup>-1</sup> and by averaging 64 scans per spectrum.

### 3.17. NO adsorption on Fe and/or Co Based SCR Catalysts

Spectroscopic NO adsorption and subsequent H<sub>2</sub>-DeNO<sub>x</sub> experiments were carried out for the verification of surface adsorption sites and thermal stability of the adsorbed species

functioning during H<sub>2</sub>-assisted NO reduction. Prior to NO adsorption (NO(g) purity, 99.9 %), each catalyst was initially annealed to 773 K in vacuum for 30 min to clean the sample surface by eliminating adsorbed atmospheric contaminants. The background IR spectrum was recorded after vacuum annealing. Then, each sample was subsequently exposed to 5.0 Torr of NO(g) for 10 min for surface saturation. The sample IR spectra were collected after evacuation of NO(g) for 20 min at 373 K in order to eliminate vibrational features associated with gas phase. Then, each NO-saturated catalyst surface was exposed to 5.0 Torr of H<sub>2</sub>(g) and temperature-dependent spectra were collected while catalyst temperature was ramped up to 673 K in H<sub>2</sub>(g) with a 12 K/min heating ramp.

### **3.18. Flow Mode Catalytic Performance Tests**

#### **3.18.1. Catalytic NO Oxidation Performance Tests on Perovskites**

Flow mode NO oxidation experiments were performed by using the custom-design plug flow reactor (described in detail in earlier sections) coupled to a T200 Teledyne NO<sub>x</sub> analyzer and MFCs. Multiple steps used in a typical NO oxidation catalytic performance test on perovskites is summarized in *Scheme 3-2*. Prior to NO oxidation experiments, each catalyst was pretreated in the presence of 5% O<sub>2</sub>/Ar at 600 K for 1 h and then 4% H<sub>2</sub>/Ar at 600 K for 1 h with 500 ml STP.min<sup>-1</sup> total flow rate. 1<sup>st</sup> NO oxidation run was carried out after the pretreatment and the 2<sup>nd</sup> NO oxidation run was executed after the ageing the catalyst at 973 K in the presence of 4% H<sub>2</sub>/Ar and this is followed by the catalytic NO oxidation performance tests.

In the catalytic performance tests, 700 ppm NO/Ar, 8 % O<sub>2</sub>/Ar with 500 ml STP.min<sup>-1</sup> total flow rate were used. The space velocity of the catalytic performance tests were reported either as Gas Hour Space Velocity (GHSV) or Volume Hour Space Velocity at STP (VHSV) or Volume Hour Space Velocity at N (VHSV) where 50,000 h<sup>-1</sup>/1,000,000 cm<sup>3</sup> STP.g<sup>-1</sup>.h<sup>-1</sup>/1,073,000 N.cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup> are calculated values for the same experiment with different units. Firstly, glass wool was inserted into the nodal (close to the downstream) point of the reactor for blank experiments. For the rest of the NO oxidation experiments, after the glass wool, 45-60 mesh 30 mg active material (perovskite or 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>) was mixed with 420 mg 45-60 mesh  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (*i.e.*, catalytically inactive filler). Sampled

gas exiting the reactor was mixed with N<sub>2</sub> for dilution, where a 1:47 dilution ratio was used to decrease NO concentration below the maximum detection upper limit of the NO<sub>x</sub> Analyzer.

The NO conversion is defined as follows:

$$NO \text{ conversion } \% = \left| \frac{(NO)_{in} - (NO)_{out}}{(NO)_{in}} \right| \times 100 \quad 3-6$$

and Specific Reaction Rate (SRR) is defined as:

$$n_{(\mu mol)} = \frac{P_{(atm)} \cdot V_{(L)}}{R \cdot T_{(K)}} \quad 3-7$$

$$SRR (\mu mol \text{ NO} \cdot g_{cat}^{-1} \cdot s^{-1}) = n_{(\mu mol)} \cdot m_{(g)}^{-1} \cdot t_{(s)}^{-1} \cdot c_{(NO)} \cdot 10^{-6} \cdot \frac{a_{(NO \%)}}{100} \quad 3-8$$

where:

$P_{(atm)}$  = Standard Pressure (1 atm)

$V_{(L)}$  = Total flow volume for 1 h

$T_{(K)}$  = Standard Temperature (273 K)

$R$  = Perfect gas constant

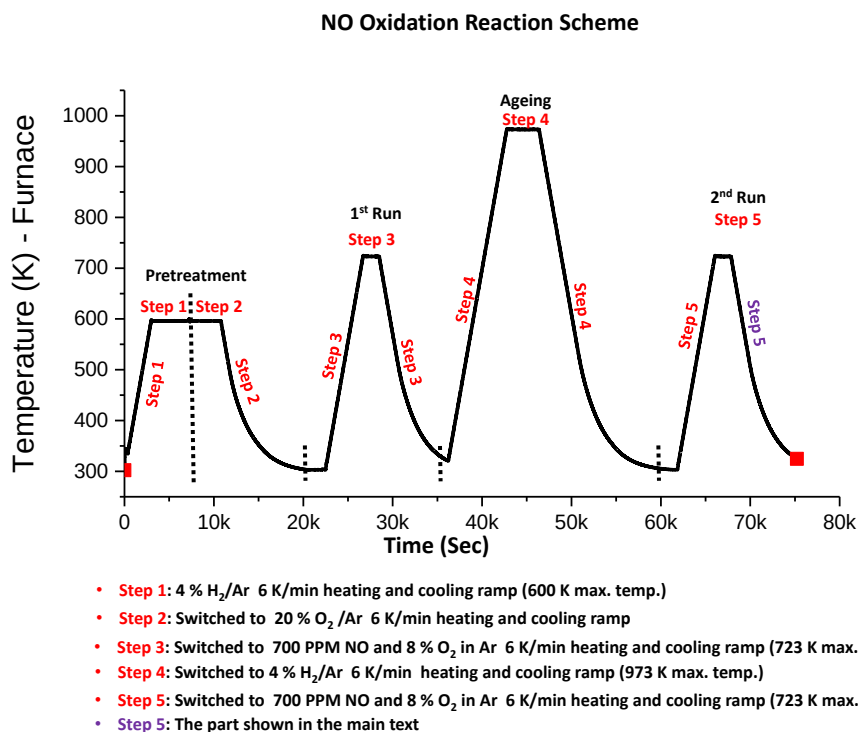
$n_{(\mu mol)}$  = Total mol number of NO flowing over the catalyst in 1 h

$m_{(g)}$  = Mass of a catalyst in g

$t_{(s)}$  = Experiment time in s for 1 h reaction time

$c_{(NO)}$  = Concentration of NO in ppm

$$a_{(NO \%)} = NO \text{ conversion } \%$$



**Scheme 3-2.** Multiple steps used in a typical catalytic NO oxidation performance test for perovskites.

### 3.18.2. Catalytic CO Oxidation Experiments on Perovskites

Flow mode CO oxidation experiments were performed by using the custom-made plug flow reactor equipped with an SRS RGA 200 QMS. Multiple steps used in a typical CO oxidation catalytic performance test on perovskites are summarized in **Scheme 3-3**. Each catalyst sample used in the CO oxidation test (*i.e.*, 210 mg 45-60 mesh  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> mixed with 45-60 mesh 40 mg active material) was pre-treated with 20% O<sub>2</sub>/Ar at 600 K for 1 h. Then, the sample was treated under 4% H<sub>2</sub>/Ar at 600 K for 1 h with a total flow rate of 500 ml STP.min<sup>-1</sup> before the activity test. After this 1<sup>st</sup> CO oxidation run, sample was aged at 973 K for 1 h in the presence of 4% H<sub>2</sub>/Ar. Then 2<sup>nd</sup> CO oxidation run was conducted on the aged sample. 1<sup>st</sup> and 2<sup>nd</sup> run of CO oxidation experiments were carried out by using 1.6 % CO and 20% O<sub>2</sub> in Ar with a heating ramp rate 4 K.min<sup>-1</sup>, where GHSV/VHSV at STP/VHSV at N was set to 100,000 h<sup>-1</sup>/750,000 cm<sup>3</sup> STP.g<sup>-1</sup>.h<sup>-1</sup>/ 805,000 N cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup> at 500 ml STP.min<sup>-1</sup> flow rate (detailed experimental procedure is shown in **Scheme 3-3**).

The CO conversion is defined as follows:

$$CO \text{ conversion } \% = \left| \frac{(CO)_{in} - (CO)_{out}}{(CO)_{in}} \right| \times 100 \quad 3-9$$

and Specific Reaction Rate (SRR) is described as:

$$n_{(\mu mol)} = \frac{P_{(atm)} \cdot V_{(L)}}{R \cdot T_{(K)}} \quad 3-10$$

$$SRR(\mu mol \text{ CO} \cdot g_{cat}^{-1} \cdot s^{-1}) = n_{(\mu mol)} \cdot m_{(g)}^{-1} \cdot t_{(s)}^{-1} \cdot c_{(CO)} \cdot 10^{-2} \cdot \frac{a_{(CO \%)}}{100} \quad 3-11$$

where:

$P_{(atm)}$  = Standard pressure (1 atm)

$V_{(L)}$  = Total flow volume for 1 h

$T_{(K)}$  = Standard temperature (273 K)

$R$  = Perfect gas constant

$n_{(\mu mol)}$  = Total mol number of CO flowing over catalyst in 1h

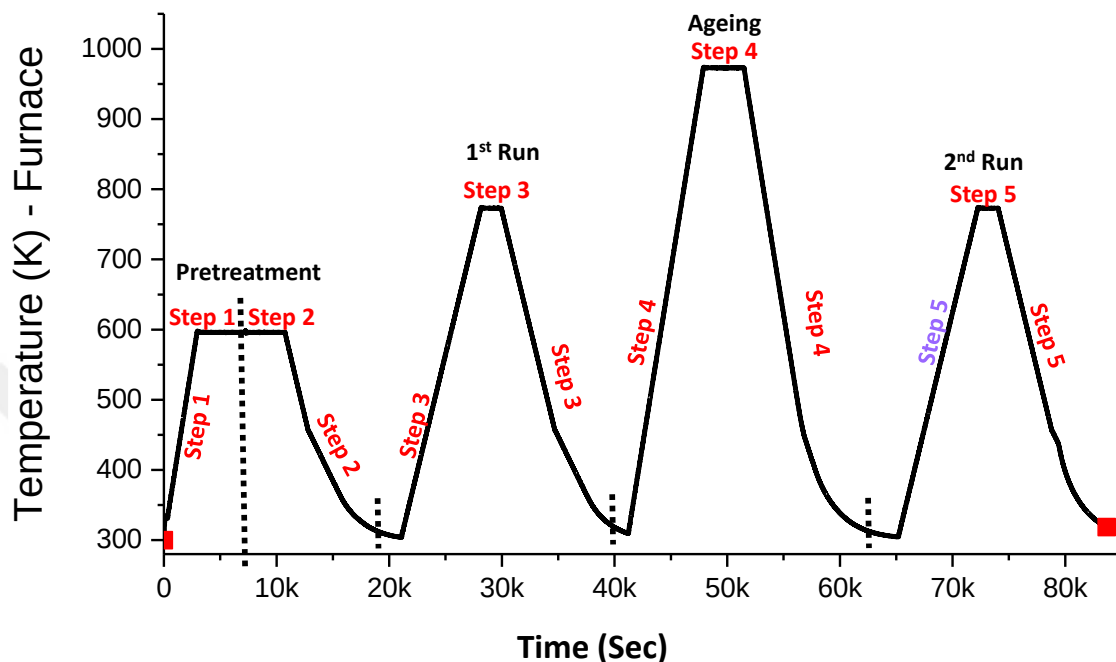
$m_{(g)}$  = Mass of a catalyst in g

$t_{(s)}$  = Experiment time in s for 1 h reaction time

$c_{(CO)}$  = CO % concentration

$a_{(CO \%)}$  = CO conversion %

## CO Oxidation Reaction Scheme



- **Step 1:** 4 % H<sub>2</sub>/Ar 6 K/min heating and cooling ramp (600 K max. temp.)
- **Step 2:** Switched to 20 % O<sub>2</sub> /Ar 6 K/min heating and cooling ramp
- **Step 3:** Switched to 1.6 CO % and 20 % O<sub>2</sub> in Ar 4 K/min heating and cooling ramp (773 K max. temp.)
- **Step 4:** Switched to 4 % H<sub>2</sub>/Ar 6 K/min heating and cooling ramp (973 K max. temp.)
- **Step 5:** Switched to 1.6 CO % and 20 % O<sub>2</sub> in Ar 4 K/min heating and cooling ramp (773 K max. temp.)
- **Step 5:** The part shown in the main text

*Scheme 3-3. Multiple steps used in a typical CO oxidation catalytic performance test for perovskites.*

Lastly, the  $m/z=28$  and  $m/z=44$  QMS channels were monitored to follow CO(g) and CO<sub>2</sub>(g) concentration variations during the CO oxidation tests. The contribution of CO<sub>2</sub> (*i.e.*, intensity of the  $m/z=44$  signal/13.5) was subtracted from  $m/z=28$  in order to account for the contribution of CO<sub>2</sub> MS fragmentation in the measured total  $m/z=28$  signal. The QMS fragmentation pattern of CO<sub>2</sub> was obtained in initial control experiments by using a CO<sub>2</sub>/Ar mixture in the absence of CO at various CO<sub>2</sub> concentrations in order to ensure that obtained CO<sub>2</sub> fragmentation coefficients are independent of the CO<sub>2</sub> concentration.

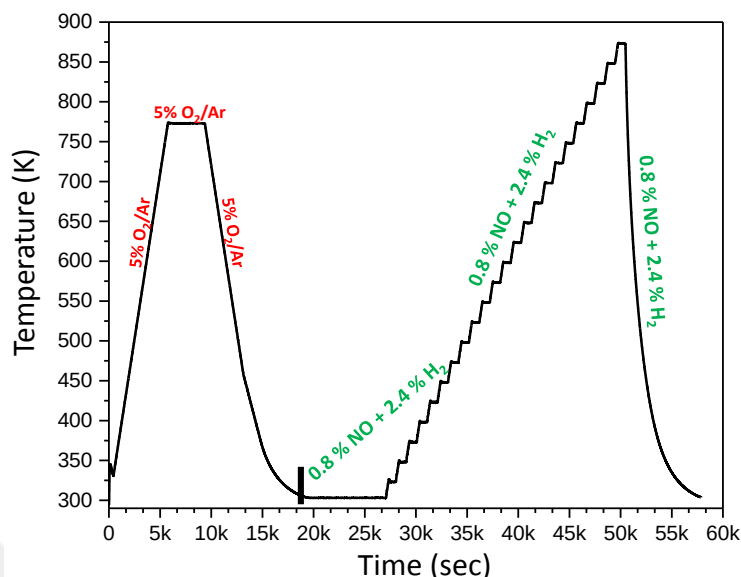
### **3.18.3. Long-Term Stability Experiments for CO & NO Oxidation Experiments**

In long-term stability experiments, each catalyst pretreated and aged by using the procedures explained in sections **3.18.1** and **3.18.2**. To obtain isothermal conditions in the catalyst bed, 50 mg of catalyst was mixed with 960 mg  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> diluent for the long-term CO oxidation experiment. The active material and diluent amount for the long-term NO oxidation experiment were kept same as it was mentioned in the main text. The long-term stability experiments were carried out isothermally at 600 K for NO oxidation reaction and at 410 K for CO oxidation reaction. Both stability tests lasted 28 h. Temperatures used in the long-term stability tests were intentionally chosen so that these values are below the corresponding temperatures for equilibrium conversion.

### **3.18.4. Flow Mode Experimental Procedure of NO Reduction with H<sub>2</sub> on Fe and/or Co Based SCR Catalysts**

#### **3.18.4.1. Temperature Dependent NO Reduction Experiments**

50 mg of a catalyst sample was first sieved by a 60-120 mesh and then placed into the flow reactor. The VHSV is set to 600.000 cm<sup>3</sup> STP.g<sup>-1</sup>.h<sup>-1</sup> where the total flow rate was fixed to 500 ml STP.min<sup>-1</sup>. In the NO reduction experiments, the initial NO(g) concentration was chosen as 0.8 % or 8000 ppm, where concentration of H<sub>2</sub>(g) was chosen to be three times higher than that of NO (*i.e.*, 2.4 % or 24000 ppm). Ar(g) was used as the balance/carrier gas. Prior to NO reduction, the samples were pretreated with 5 % O<sub>2</sub>/Ar 500 at 773 K for 1 h with a heating ramp of 5 K/min. Then the system was cooled down to room temperature (RT) and the NO mixture mentioned above was exposed to the reactor for 1 h to stabilize all MS signals. After signal stabilization, the catalyst temperature was raised by using 25 K steps with a 5 K/min ramp and a 12 min soak at a given temperature (**Scheme 3-4**). After reaching 873 K (*i.e.*, the maximum temperature), system was cooled to RT under ambient conditions (without using an additional cooling system).



**Scheme 3-4.** The schematic demonstration of the temperature profile and the gas mixtures used in a typical NO reduction experiment.

#### 3.18.4.2. Data Analysis in NO Reduction Experiments

SRS RGA200 QMS mass spectrometer was used to follow the alteration of the reactants and products in the NO reduction experiments (Chemiluminescence  $\text{NO}_x$  Analyzer is highly sensitive to  $\text{NH}_3$  which leads to improper detection of  $\text{NO}_x$ ). The possible products such as  $\text{N}_2\text{O}$  ( $m/z=44$ ),  $\text{NH}_3$  ( $m/z=15$  was followed rather than 17 due to spectral overlap), and  $\text{N}_2$  ( $m/z=28$ ) were monitored along with reactant NO ( $m/z=30$ ) and  $\text{H}_2$  ( $m/z=2$ , not used in the data analysis).  $\text{H}_2$  consumption occurs as a function of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  production. The H balance in between product and reactants could be beneficial to address  $\text{NH}_3$  or  $\text{H}_2\text{O}$  selectivity. However, high condensation probability of water on cold spots in the pipeline before reaching to the detector, complexity of water concentration calibration with mass spectrometer, and unstable water background in mass spectrometer obstruct the accurate detection of water as a product. Hence, only N contained products were used in data analysis. Before the experiments, QMS signals of each of the investigated species were stabilized to obtain steady-state values which are used as the background (*i.e.*, baseline) values for these species. Upon subtraction of these background signals from each investigated QMS channel, a “zero” starting signal intensity is obtained for each species. Then, each signal was multiplied with the relevant correction coefficients obtained from the QMS fragmentation patterns of corresponding species. Note that the fragmentation

patterns of each of these species were initially obtained before the catalytic performance tests by performing calibration experiments in the absence of other species except Ar. Concentration of the calibrated species was varied in order to ensure that fragmentation patterns are independent of concentration.

Thus, following correction coefficients were obtained and each signal is divided with the corresponding coefficient to estimate unfragmented magnitude of each QMS signal:

- ❖ NO coeff = 0.96
- ❖ N<sub>2</sub> coeff = 0.96
- ❖ N<sub>2</sub>O coeff = 0.466
- ❖ NH<sub>3</sub> coeff (m/z=15) = 0.022

N<sub>2</sub>O fragmentation (*i.e.*, NO and N<sub>2</sub>) contributions should also be subtracted from NO and N<sub>2</sub> signals, where NO and N<sub>2</sub> contributions from N<sub>2</sub>O can be found by multiplying the N<sub>2</sub>O signal with the coefficients 0.4596 and 0.0387, respectively.

Finally, nitrogen atom balance (*i.e.*, N mass balance) can be considered by counting total number of N-atoms in products and reactants (here, the N<sub>2</sub> and N<sub>2</sub>O signals should be further multiplied with a factor of two as they contain two nitrogen atoms per molecule). These considerations are expressed mathematically below. In these expressions ionization current (IC) represents the amplitude of the QMS signal.

$$a = \text{Quantity of } N_2O = (IC_{raw}44 - IC_{bg}44)/0.466 \quad 3-12$$

$$b = \text{Quantity of } N_2 = (IC_{raw}28 - IC_{bg}28)/0.96 - a * 0.03837 \quad 3-13$$

$$c = \text{Quantity of } NO = (IC_{raw}30 - IC_{bg}30) * 0.96 - a * 0.4596 \quad 3-14$$

$$d = \text{Quantity of } NH_3 = ((IC_{raw}15 - IC_{bg}15) - c * 0.0131) * 0.022 \quad 3-15$$

The nitrogen mass balance for a given temperature can be expressed as:

$$c = (a * 2) + (b * 2) + (d) \quad 3-16$$

Where IC<sub>raw</sub> is the raw QMS signal without any numerical manipulation and IC<sub>bg</sub> are the background QMS signals in the “idle” reactor prior to dose of any species other than Ar.

### The NH<sub>3</sub> case:

In the NO(g) reduction experiments H<sub>2</sub>O formation is expected as a side product. Hence, the QMS fragmentation of H<sub>2</sub>O (m/z=18) to form OH (m/z=17) leads to a significant overlap with the molecular ion of NH<sub>3</sub> (m/z=17). The strong ammonia QMS fragmentation signal due to NH<sub>2</sub> (m/z=16) also overlaps with that of O and thus cannot be used to quantify ammonia. Thus, a weaker QMS fragmentation signal of ammonia at m/z=15 (due to NH) was chosen to monitor and quantify NH<sub>3</sub> generation where NH (m/z=15) signal should be divided by 0.022 to obtain the true magnitude of the NH<sub>3</sub> signal. As an interesting complication, NO(g) has also a minor contribution to the m/z=15 signal. At a first glance, NO is expected to reveal only m/z =14, 16 fragmentation signals due to the formation of atomic N and O. However, atomic N can further interact with H-containing species in the vacuum background such as water to form a small quantity of NH (m/z=15). Note that the isotopic abundance of <sup>15</sup>N in nature is typically <0.4%, so its contribution is neglected. Thus, about 1.3 % of the original NO molecules lead to an NH signal. While this latter signal might be small, due to the already small NH signal coming from ammonia, this correction is significant and needs to be made. This correction is also graphically illustrated in **Figure 3-1**.

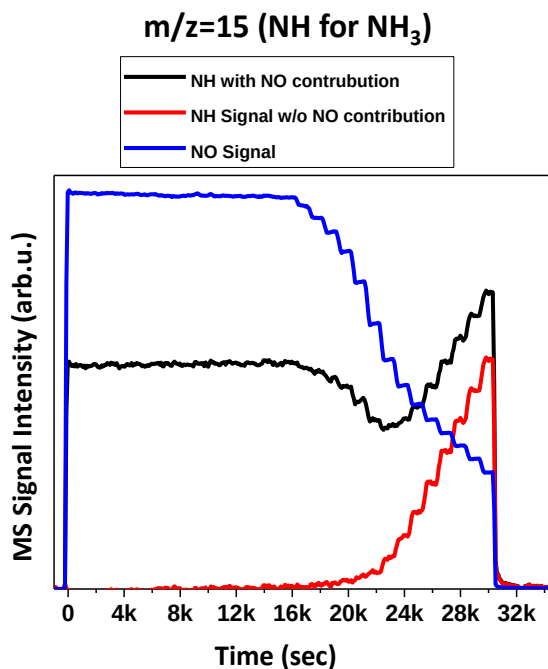
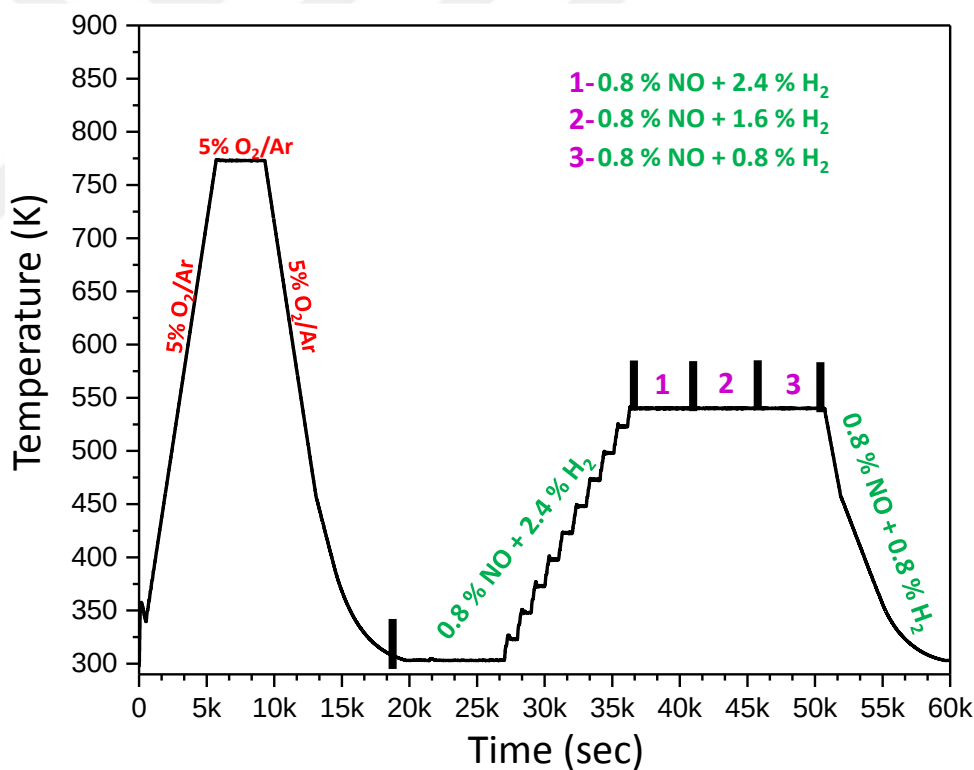


**Figure 3-1.** Comparison of NH (m/z=15) signals with (black) and without (red) contribution from NO fragmentation and further reaction with background water to form NH (m/z=15). Corresponding NO (m/z=30) signal is also shown (blue-line).

### 3.18.4.3. Catalytic NO reduction Performance Tests at Various H<sub>2</sub> Concentrations

The experimental procedure described in section 3.18.4.2 was maintained for NO reduction experiments with a few changes. In order to study the effect of hydrogen concentration on the NO reduction performance, reaction temperature was chosen as the temperature (*i.e.*, T<sub>50</sub>), where 50% NO conversion is achieved for 0.8% NO + 2.4% H<sub>2</sub> feed mixture (rather than 873 K). Then, at T<sub>50</sub>, 24000, 16000 and 8000 ppm H<sub>2</sub> concentrations were used in the tests by keeping NO concentration constant. NO reduction reaction was executed for a duration of 60 min for each H<sub>2</sub> concentration. Other experimental parameters such as the total gas flow rate, VHSV, catalyst amount, pretreatment and data analysis are kept identical with the parameters defined in section 3.18.4.2.



**Scheme 3-5.** The experimental procedure for NO reduction catalytic performance tests at various H<sub>2</sub> concentrations.

As seen in **Scheme 3-5**, the stoichiometric NO:H<sub>2</sub> ratio of 1:3 was utilized at T<sub>50</sub> at the beginning of the NO reduction reaction for 1 h. Then, hydrogen supply was restricted to set NO:H<sub>2</sub> ratio to 1:2, and 1:1.

## CHAPTER 4

### 4. Results and Discussion

#### 4.1. Perovskite Based DOC Catalysts

##### 4.1.1. Elucidation of Perovskite Structure using *Ex-situ* Characterization Methods

**Figure 4-1** indicates the XRD profiles of  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$ , and selected B-site mixed  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  perovskites along with their reference XRD patterns (*shown in red*) corresponding to the relevant Joint Committee on Powder Diffraction Standards (JCPDS) cards supplied by the International Centre for Diffraction Database (ICDD). Upon monitoring the structural evolution of the XRD patterns of all of the 11-different synthesized B-site mixed  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  samples (see **Appendix A1**), where  $x$  ranged within  $0.1 \leq x \leq 0.9$ , we observed a gradual transformation of the XRD patterns from that of  $\text{LaCoO}_3$  to  $\text{LaMnO}_3$  with increasing Mn loading. In all these cases, perovskite structure was clearly detectable with varying polymorphs. This important observation is consistent with the existence of a B-site mixed bulk perovskite structure, where both  $\text{Mn}^{+x}$  and  $\text{Co}^{+x}$  cations mostly co-exist in the same unit cell rather than forming two entirely distinct perovskite structures. This finding is in accordance with a multitude of other experiments that will be provided in the rest of the current work. As, it is discussed in the forthcoming sections,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  B-site mixed perovskites revealed the highest reactivity and thus, they were studied and discussed in detail in the following sections.

Each diffraction pattern in **Figure 4-1** was recorded after synthesis and calcination in air at 973 K for 5 h. The primary diffraction signal of  $\text{LaMnO}_3$  at  $2\theta = 32.5^\circ$  indicates the presence of a cubic perovskite structure, whereas for  $\text{LaCoO}_3$ , appearance of a doublet at  $32.9^\circ$  and  $33.3^\circ$  suggests the existence of a rhombohedral perovskite structure [182], [183].

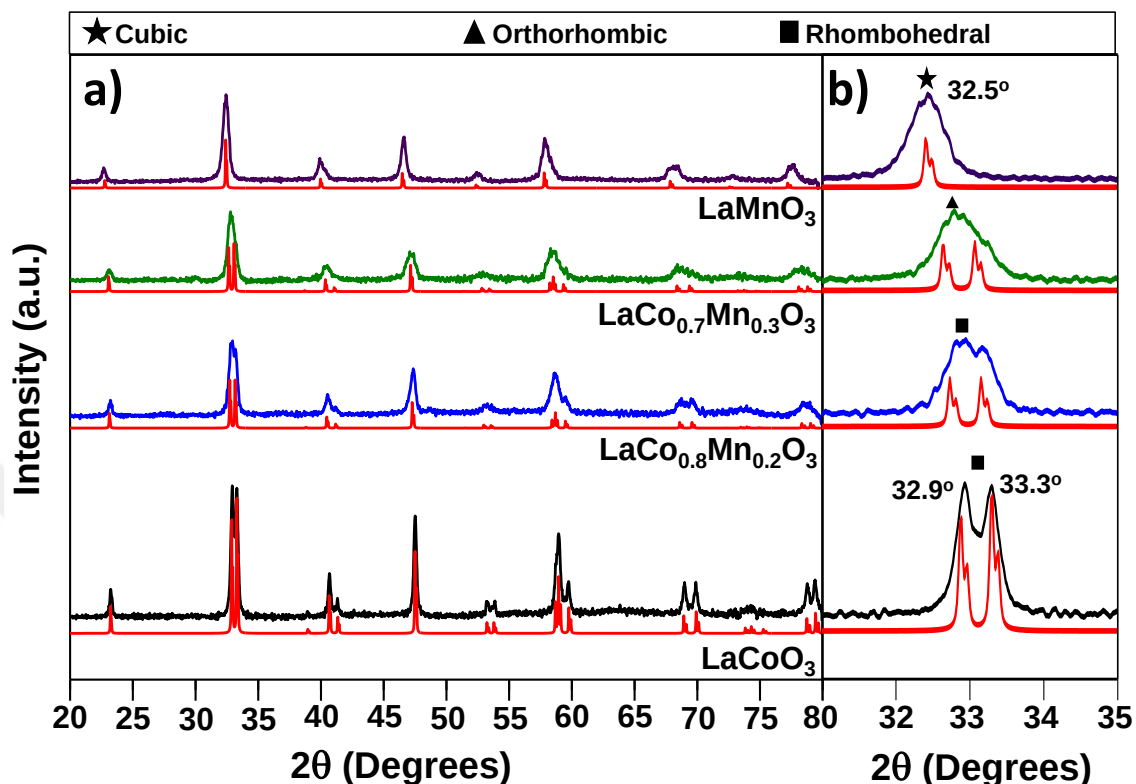


**Figure 4-1.** a) XRD profiles of  $\text{LaMnO}_3$  (PDF Card No: 04-006-9518),  $\text{LaCoO}_3$  (PDF Card No: 00-048-0123),  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  (PDF Card No: 04-012-5614) and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  (PDF Card No: 04-012-5615) samples after calcination at 973 K for 5 h. b) Detailed views of the XRD patterns for  $31^\circ < 2\theta < 35^\circ$ .

It is apparent that Mn addition to the  $\text{LaCoO}_3$  structure with increasing loadings (i.e., for  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ) leads to a monotonic shift of the  $\text{LaCoO}_3$  primary diffraction signals at  $32.9^\circ$  and  $33.3^\circ$  towards lower angles and convergence of the doublet signals to form a broader singlet signal. As shown in **Figure 4-1**, crystal structures of  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  B-site mixed perovskite systems are assigned as rhombohedral (ICDD Pdf Card No: 04-012-5615) and orthorhombic (ICDD Pdf Card No: 04-012-5614), respectively. These observations are consistent with the transformation of the rhombohedral  $\text{LaCoO}_3$  perovskite structure first into the orthorhombic and then to the cubic structure in a gradual fashion upon doping with increasing loadings of Mn. XRD pattern of  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  also resembles to that of a cubic structure. However, broadening of the main diffraction signal at  $33^\circ$  and the appearance of the weak diffraction peak at *ca.*  $69^\circ$  is in line with the orthorhombic structure.

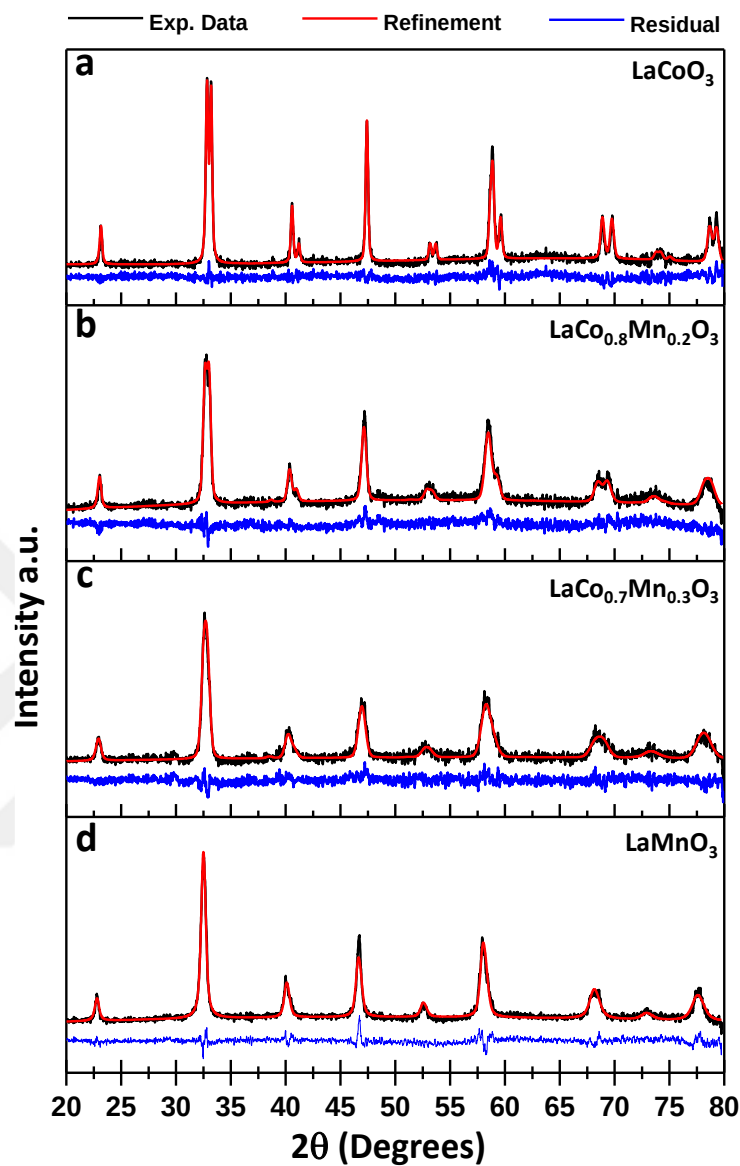


**Figure 4-2.** XRD Rietveld refinement results for a)  $\text{LaCoO}_3$ , b)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , c)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaMnO}_3$ .

**Table 4-1.** XRD Rietveld refinement parameters.

| Perovskite Samples<br>(XRD Rietveld Refinement) | Refined Parameters |        |        |       |
|-------------------------------------------------|--------------------|--------|--------|-------|
|                                                 | Rexp %             | Rwp %  | Rb %   | Sig   |
| $\text{LaCoO}_3$                                | 2.848              | 2.897  | 2.202  | 1.017 |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$    | 6.338              | 12.160 | 11.919 | 1.919 |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$    | 6.480              | 11.537 | 9.319  | 1.780 |
| $\text{LaMnO}_3$                                | 4.204              | 4.235  | 3.744  | 1.007 |

**Table 4-2.** Lattice parameters and average crystallite sizes of the perovskites based on Rietveld refinement results.

| Perovskite Samples<br>(XRD Rietveld Refinement)      | Lattice Parameters |       |        |          |         |          | Average Crystallite Size (nm) |
|------------------------------------------------------|--------------------|-------|--------|----------|---------|----------|-------------------------------|
|                                                      | a (Å)              | b (Å) | c (Å)  | $\alpha$ | $\beta$ | $\gamma$ |                               |
| LaCoO <sub>3</sub>                                   | 5.448              | 5.448 | 13.128 | 90       | 90      | 120      | 92.5±1.5                      |
| LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub> | 5.479              | 5.479 | 13.204 | 90       | 90      | 120      | 54.6±1.2                      |
| LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub> | 5.497              | 5.497 | 13.266 | 90       | 90      | 120      | 59.7±3.2                      |
| LaMnO <sub>3</sub>                                   | 3.882              | 3.882 | 3.882  | 90       | 90      | 90       | 29.5±3.2                      |

XRD Rietveld refinement for perovskite samples were performed by MAUD [184] software, results and refined parameters were demonstrated in **Figure 4-2**, **Table 4-1**, and **Table 4-2**. Based on XRD experimental results and advanced analysis of the crystal structure data (Rietveld refinement), no other additional metal oxide or metal hydroxide bulk phases such as La<sub>2</sub>O<sub>3</sub>, CoO<sub>x</sub>, MnO<sub>x</sub>, La(OH)<sub>3</sub>, Co(OH)<sub>x</sub>, Mn(OH)<sub>x</sub> etc. were detectable in the XRD patterns. However, existence of such minority domains (particularly on the surface of the catalysts rather than in the bulk) cannot be ruled out.

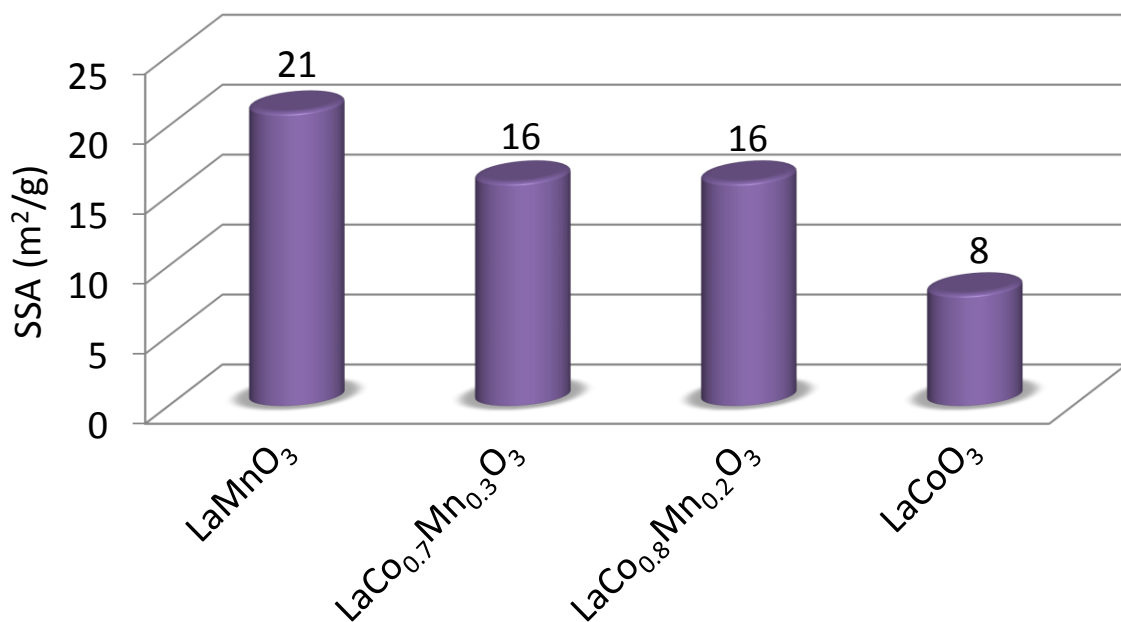


**Figure 4-3.** Specific surface area (SSA) values for LaMnO<sub>3</sub>, LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub>, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> and LaCoO<sub>3</sub> samples after calcination at 973 K for 5 h.

SSA values of the investigated perovskites are presented in **Figure 4-3**. In addition, SSA values of all of the currently synthesized 11-different LaCo<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub> samples within  $0 \leq x$

$\leq 1.0$  are also given in **Appendix A2**.  $\text{LaMnO}_3$  reveals a relatively higher SSA ( $21 \text{ m}^2/\text{g}$ ) than that of  $\text{LaCoO}_3$  ( $8 \text{ m}^2/\text{g}$ ), while SSA of B-site mixed perovskites are located in between these two extremes. SSA values of these  $\text{LaMnO}_3$  and  $\text{LaCoO}_3$  samples are consistent with the former studies in the literature [185]–[187]. It is apparent that the increasing Mn loading in the B-site mixed perovskite structure typically tends to increase the SSA. This is in good accordance with the crystallographic changes observed as a function of perovskite composition (**Figure 4-1**), where increasing Mn loading leads to a gradual transformation from rhombohedral to cubic crystal structure. Thus, current XRD and BET analysis clearly show that crystal structure and surface area of the B-site mixed perovskites can be fine-tuned by controlling the synthesis conditions and nominal Mn/Co precursor loadings.

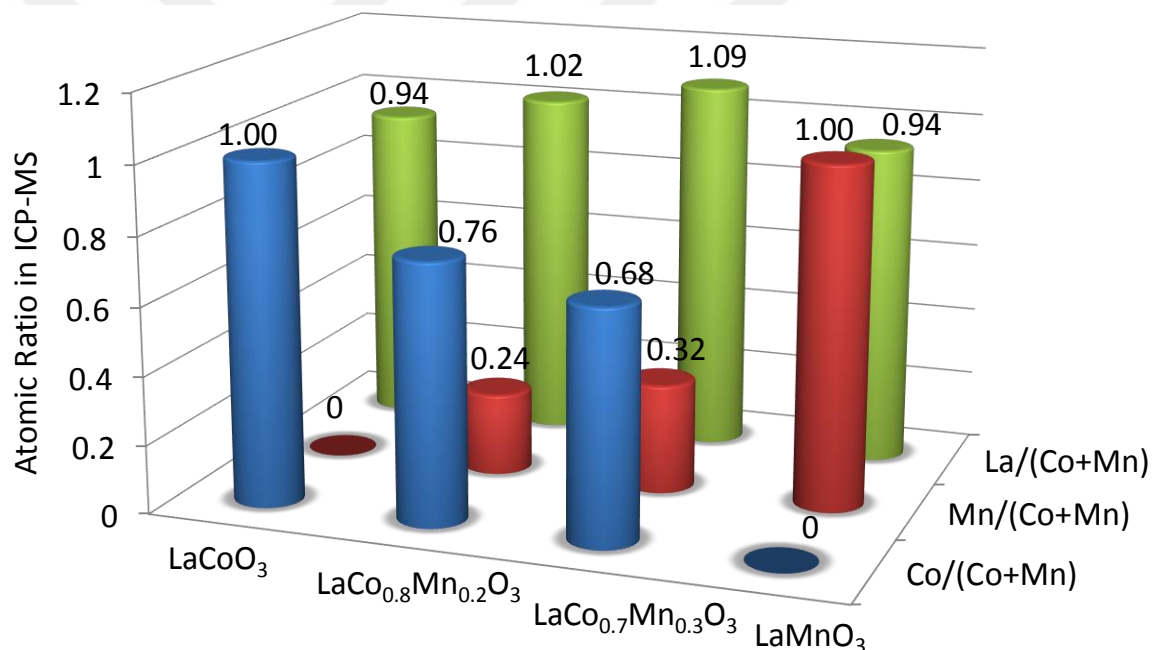


**Figure 4-4.** Bulk compositional analysis of the selected perovskite samples with ICP-MS. The foremost set of histograms (blue) represent the relative number of Co cations with respect to the total number of B-site cations (i.e.,  $\text{Co}/(\text{Co}+\text{Mn})$ ), middle set of histograms (red) correspond to the  $\text{Mn}/(\text{Co}+\text{Mn})$  cation ratio and the rearmost histograms (green) depict the ratio of the A site cations to the total B site cations (i.e.,  $\text{La}/(\text{Co}+\text{Mn})$ ).

**Figure 4-4** shows the bulk compositional analysis of the selected perovskite samples as measured with ICP-MS measurements. It also depicts the relative population of the B-site cations in terms of Co (i.e.,  $\text{Co}/(\text{Co}+\text{Mn})$ ) or Mn (i.e.,  $\text{Mn}/(\text{Co}+\text{Mn})$ ), as well as the relative abundance of A site cations with respect to that of total number of B-site cations (i.e.,  $\text{La}/(\text{Co}+\text{Mn})$ ). **Figure 4-4** and **Table 4-3** show that experimentally determined bulk atomic ratios of the A and B-site cations are in very good agreement with the nominal

compositions estimated by the corresponding precursor amounts used in the synthesis. In order to demonstrate the reproducibility of the ICP-MS measurements, two independent samples were taken for each perovskite, where each of these samples were measured 5 times. Deviations from the mean values were typically < 1 % as shown in **Appendix A3**. It is worth mentioning that one cannot precisely comment on the bulk oxygen contents of these materials solely based on ICP-MS data, since ICP-MS technique only reveals information about the cations present in the bulk structure. However, the relative oxygen contents of these materials can be estimated by combining cation concentration in the bulk by the ICP-MS technique and bulk oxidation state of the cations by XANES data.

**Table 4-3.** Nominal (based on metal precursor amounts used in synthesis) and experimental (ICP-MS-based) relative bulk cation compositions of investigated perovskites.

| Nominal composition estimated by the precursor amounts used in the synthesis | Bulk composition estimated via ICP-MS data by normalizing the total A and B-site composition to 2.00* |
|------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| $\text{LaCoO}_3$                                                             | $\text{La}_{0.97}\text{Co}_{1.03}\text{O}_{3+\alpha}$                                                 |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$                                 | $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{3+\alpha}$                                 |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$                                 | $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{3+\alpha}$                                 |
| $\text{LaMnO}_3$                                                             | $\text{La}_{0.97}\text{Mn}_{1.03}\text{O}_{3+\alpha}$                                                 |

\* This set of empirical formulas will be used for the calculation of « $\alpha$ » values in combination with the current XANES data.

**Figure 4-4** reveals a relatively low La content in bulk structure of simple perovskites with a single type of B-site cation such as  $\text{LaCoO}_3$  or  $\text{LaMnO}_3$  as compared to the B-site mixed perovskites. La-deficiency in these simpler perovskites can be attributed to the presence of a greater extent of A-site bulk vacancies in these materials as compared to the B-site mixed perovskites. A-site bulk vacancies of La-based perovskites have also been reported in various former reports in the literature [188], [189]. For instance, Mizusaki *et al.* reported that La-based simple perovskites synthesized using the co-precipitation method at  $T \leq 900$  °C typically revealed La-deficiency in the bulk [188]. Our results in **Figure 4-4** and **Table 4-3** suggest that alterations of the type, size and oxidation state of the B-site cations have measurable influences on the A-site vacancies as well as the perovskite stoichiometry.

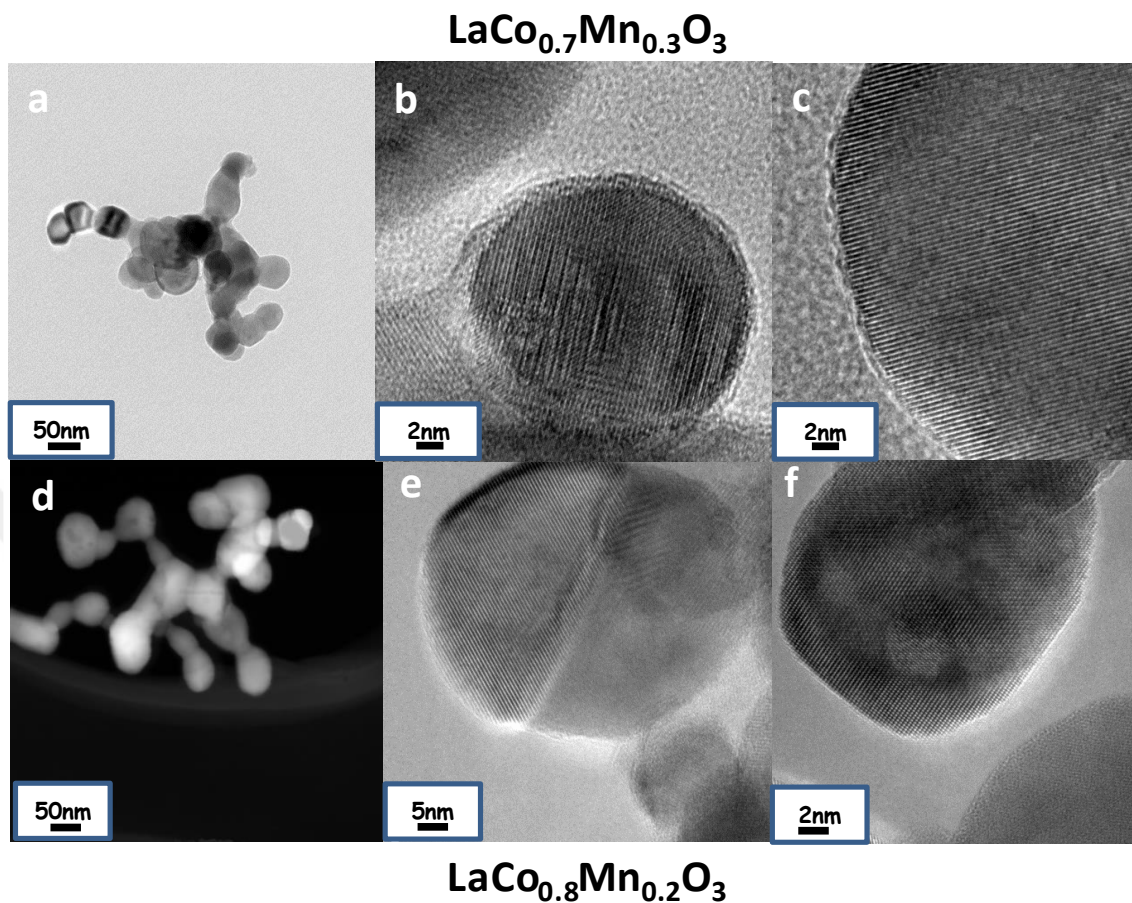


**Figure 4-5.** TEM images of  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  (a-c) and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  (d-f).

**Figures 4-5a-5f** present TEM images of  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  B-site mixed perovskites. It is apparent that the average particle size of these perovskites range within 40-60 nm (**Figures 4-5a** and **5d**). TEM images in **Figures 4-5a** and **5d** suggest low-porosity for these materials on a given region due to well-ordered crystalline patterns. Atomically well-ordered and crystalline nature of these perovskites can also be seen in higher resolution images (**Figures 4-5c** and **5f**). These observations are consistent with the relatively low SSA values (**Figure 4-3**) of these materials. TEM results of the currently presented B-site mixed perovskites are comparable to that of the simple perovskites (*i.e.*,  $\text{LaCoO}_3$  or  $\text{LaMnO}_3$ ) reported in one of our former reports [185].

For the quantification of the surface composition of the investigated perovskites, XPS measurements were performed. **Figures 4-6a** and **6b** show Co 2p and Mn 2p XP spectra of selected perovskite samples, respectively. Spectra in **Figure 4-6a** were normalized with respect to the corresponding intensity of the  $\text{LaCoO}_3$  spectrum. Likewise,  $\text{LaMnO}_3$

spectrum was used in the intensity normalization of the XPS data in **Figure 4-6b**. In **Figure 4-6a**, Co 2p<sub>3/2</sub> binding energy (B.E.) of LaCoO<sub>3</sub> sample at 780.8 eV can be attributed to the Co<sup>3+</sup> and/or Co<sup>2+</sup>/Co<sup>3+</sup> states [190]–[193]. Although Co 2p<sub>3/2</sub> B.E. for pure Co(II) oxide (CoO) was also reported in the literature at a B.E. of 780-781 eV. The lack of the satellite signal at *ca.* 786 eV suggests that Co<sup>3+</sup> is the prominent species on the surface of LaCoO<sub>3</sub> [192], [194]. It was also reported in the literature that Co<sub>3</sub>O<sub>4</sub> has a smaller satellite (compared to CoO) at *ca.* 789 eV [191]. Such a satellite is also discernable at 790 eV in **Figure 4-6a** indicating the co-presence of Co<sup>2+</sup>/Co<sup>3+</sup> states on LaCoO<sub>3</sub>. **Figure 4-6a** reveal that Co 2p<sub>3/2</sub> B.E. at 780.8 eV shifts to lower B.E. and appears at 780.3 eV with increasing Mn loading. This is in accordance with the reduction of the surface Co cations due to Mn addition. A higher oxygen affinity of the Mn sites in Co-Mn bimetallic nanoparticles was reported in a former study [190]. Thus, relatively higher oxygen affinity of Mn cations may facilitate the reduction of the Co cationic sites on the surface of the B-site mixed perovskites. It is worth mentioning that observed variations in the Co 2p<sub>3/2</sub> B.E. as a function of perovskite composition is in good accordance with the modification of the B-site electronic structure and the existence of a B-site mixed perovskite system.

In **Figure 4-6b**, Mn 2p<sub>3/2</sub> B.E. is observed at 642.2 eV for the LaMnO<sub>3</sub> sample. This signal can be attributed to Mn<sup>4+</sup> in agreement with the literature [190], [191]. Excess positive charge on the surface due to Mn<sup>4+</sup> sites could be electrically compensated by additional oxide ions. No detectable B.E. shift was observed in the Mn 2p<sub>3/2</sub> signal of the B-site mixed (LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> and LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub>) perovskite samples as compared to that of LaMnO<sub>3</sub> (**Figure 4-6b**). This observation suggests that either the associated Mn B.E. shifts are too small to be detected with the currently available XP energy resolution or the presence of Co sites in the perovskite structure does not significantly alter the oxidation state of the surface Mn sites from Mn<sup>4+</sup>. Thus, it is not possible to entirely rule out the presence of surface Mn<sup>3+</sup> (minority) states based on the current XPS results.

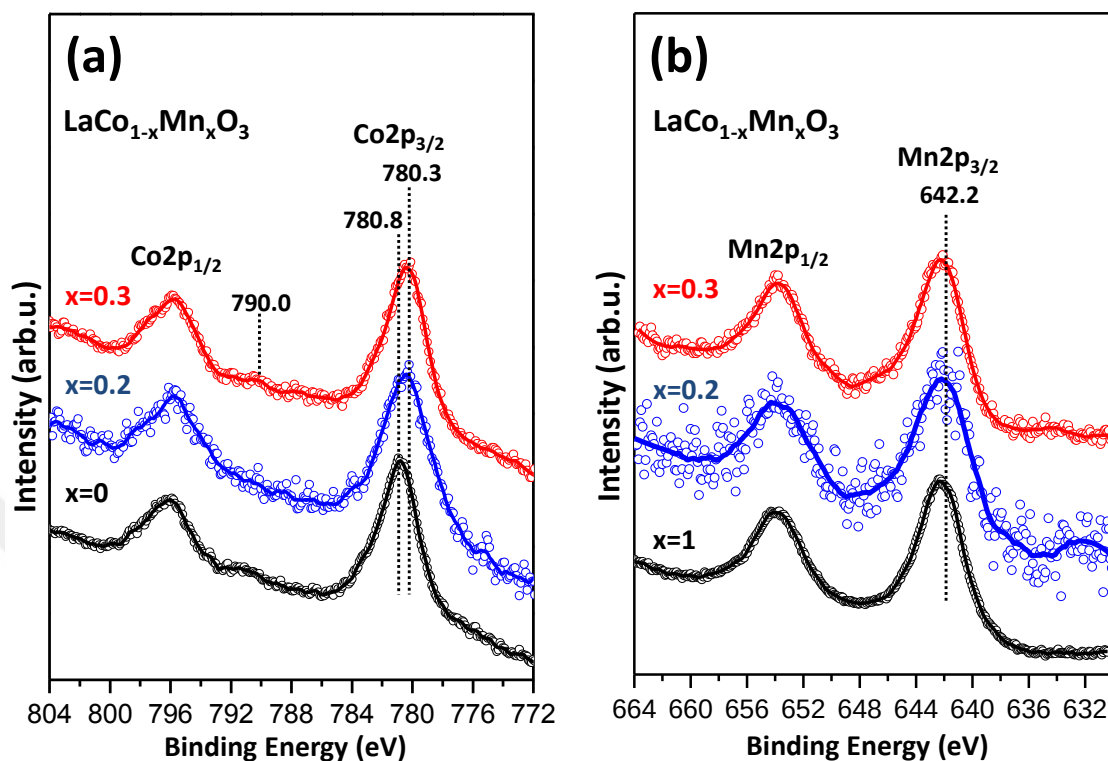


**Figure 4-6.** Co 2p (a) and Mn 2p (b) XP spectra of selected perovskites as a function of increasing or decreasing “x” in nominal composition.

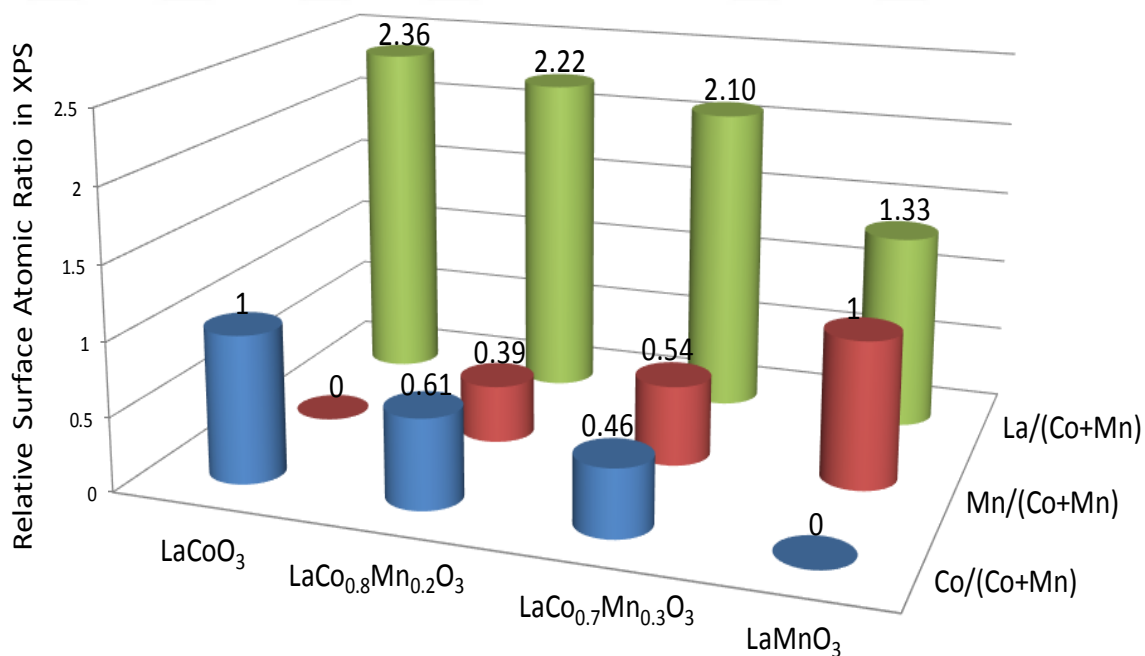


**Figure 4-7.** Surface atomic ratios (Co/(Co+Mn), blue; Mn/(Co+Mn), red; La/(Co+Mn), green) for selected perovskites obtained via XPS.

Surface compositions of the selected perovskites in terms of A-site and B-site cations were also investigated *via* XPS. Relative abundance of Co or Mn with respect to the total B-site cations (*i.e.*,  $\text{Co}/(\text{Co}+\text{Mn})$  and  $\text{Mn}/(\text{Co}+\text{Mn})$ ) and the ratio of A-site cations to the total B-site cations (*i.e.*,  $\text{La}/(\text{Co}+\text{Mn})$ ) on the surfaces of  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  samples are given in **Figure 4-7**. It is apparent that all samples reveal excess La on their surfaces. This is consistent with a former theoretical study [195] suggesting that analogous perovskites have La termination on their surfaces as well as a former experimental XPS study on  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  reporting excess La on the surface [185].  $\text{Co}/(\text{Co}+\text{Mn})$  and  $\text{Mn}/(\text{Co}+\text{Mn})$  ratios corresponding to the surface of the perovskites obtained *via* XPS are slightly different than that of the bulk values obtained *via* ICP-MS (**Figure 4-4**), however general trends are rather similar in both sets of data, exhibiting increasing Co surface concentration with increasing nominal Co loading. On the other hand, it is clear that overall surface compositions (**Figure 4-7**) of all of the investigated perovskites are much more complex than that of the bulk compositions (**Figure 4-4**), when corresponding values for La, O, and C are also taken into consideration. The presence of significantly excess amounts of surface La, C and O species in XPS spectra (data not shown) indicates the possibility of the existence of additional surface species such as  $\text{La}_2\text{O}_3$ ,  $\text{La}(\text{OH})_3$ ,  $\text{La}_2(\text{CO}_3)_2$ ,  $\text{CoO}_x$ ,  $\text{MnO}_x$ ,  $\text{Co}(\text{OH})_x$ ,  $\text{Mn}(\text{OH})_x$ ,  $\text{Co}(\text{CO}_3)_x$ ,  $\text{Mn}(\text{CO}_3)_x$  which could be elusive to detect with bulk spectroscopic techniques due to their low concentrations. It is worth mentioning that the excess amounts of oxygen and carbon can be associated at least in part to surface  $\text{H}_x\text{C}_y\text{O}_z$  species, which may possibly originate from the organic residues of the synthesis chemicals used in the citrate method, which were not completely removed from the surface upon calcination.

*Ex-situ* XANES experiments were performed to examine the bulk composition and the average oxidation states of B-sites in the currently investigated perovskite samples. Mn K-edge and Co K-edge energy shifts in the B-site mixed and simple perovskites were determined by experimentally referencing these energy values with respect to their metallic foils. Therefore, corresponding Mn and Co metal foils (Mn 6539 eV, Co 7709 eV) were also recorded simultaneously during each sample spectrum acquisition. Inflection point of the main edge was identified as the edge energy ( $E_0$ ) [196]–[198].

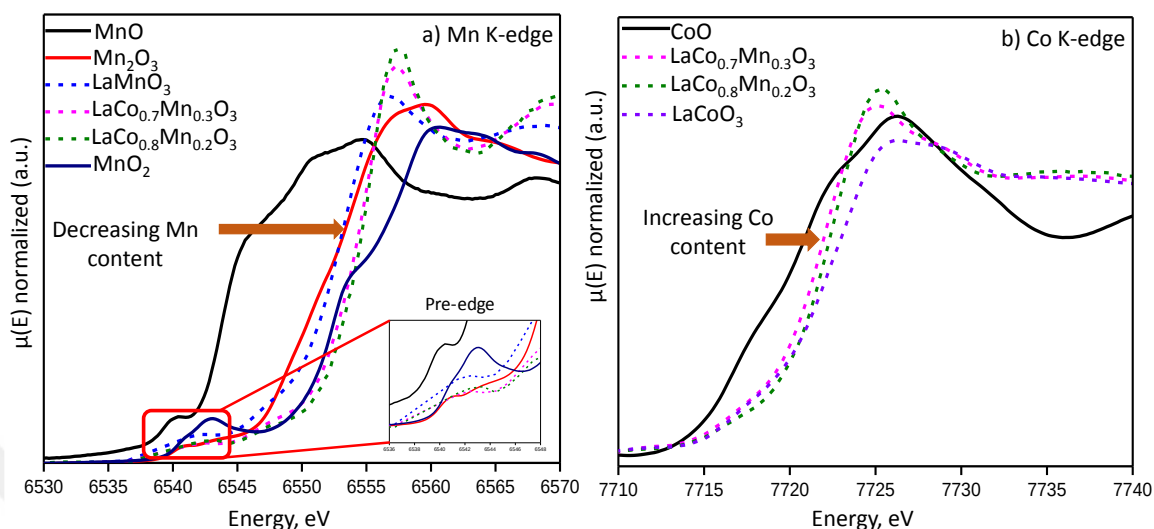


**Figure 4-8.** Ex-Situ XANES results for the Mn K-edge of a) MnO,  $\text{Mn}_2\text{O}_3$ ,  $\text{LaMnO}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , and  $\text{MnO}_2$ ; b) Co K-edge of  $\text{CoO}$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , and  $\text{LaCoO}_3$ .

**Figure 4-8a** and **8b** present the normalized X-ray absorption spectra, where each sample was measured three times and then an average spectrum was obtained for each sample. Edge positions of all samples/reference foils were found to be reproducible with a variation of less than 0.1 eV. In **Figure 4-8a**,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  (6555.6 eV) shows the highest Mn-K edge energy value revealing the highest bulk Mn oxidation state among the investigated perovskites. Mn-K edge energy of  $\text{LaMnO}_3$  was measured at 6553.2 eV. This value shifted to slightly higher values of 6555.5 and 6555.6 eV for  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , respectively. Former XANES/EXAFS and NMR studies on  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ -type perovskites reported that average bulk oxidation state of Mn increased with decreasing Mn content, while average bulk oxidation state of Co increased with increasing Co content [199]–[204]. Results presented in **Figure 4-8** are in good accordance with these former findings. Additionally, inset of **Figures 4-8a** presents the pre-edge features of Mn-K edge due to 1s-3d forbidden transition and it is sensitive to filling rate of 3d level [209]. The lower intensity of the perovskites as compared to  $\text{MnO}_2$  point out that perovskites Mn contain cations with lower oxidation state than +4 and it is compatible with the calculation with using edge of 1s-4p (k-edge) absorption.

Charges of the Mn and Co cations are essential for the redox characteristics of perovskites. Sikora *et al.* reported that  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  type perovskites have  $\text{Mn}^{4+}/\text{Mn}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$

mixed oxidation states and the average oxidation state of both Mn and Co increased linearly as a function of Co content in the perovskite structure [201]. Additionally, other reports also confirmed the coexistence of  $\text{Mn}^{4+}/\text{Mn}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$  mixed oxidation states in  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  [203], [205]. The crystal structure of the currently synthesized  $\text{LaCoO}_3$  is rhombohedral (see **Figure 4-1**). This can be associated to the distortion of the  $\text{CoO}_6$  octahedra in the unit cell and presence of high-spin state  $\text{Co}^{3+}$  as the prevalent species in the crystal structure [206]. **Figure 4-8b** shows the Co K-edge XANES spectra of  $\text{CoO}$  ( $\text{Co}^{2+}$ ),  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCoO}_3$ , where  $E_0$  values were determined to be 7719.5, 7722.1, 7722.7, and 7723.3 eV; respectively (**Table 4-4**). As the Mn content increases (i.e., Co content decreases), Co K-edge shifts to the relatively lower energies suggesting that Mn addition reduces  $\text{Co}^{3+}$  cation in the bulk of the perovskite architecture. These values (**Table 4-4**) are consistent with the current XPS results (**Figure 4-6**), as well as former XANES studies on cobalt oxides, where Co K-edge values were reported to be 7718.2 eV for  $\text{Co}^{2+}$  and 7724.0 - 7724.7 eV for  $\text{Co}^{3+}$  [206]–[208].

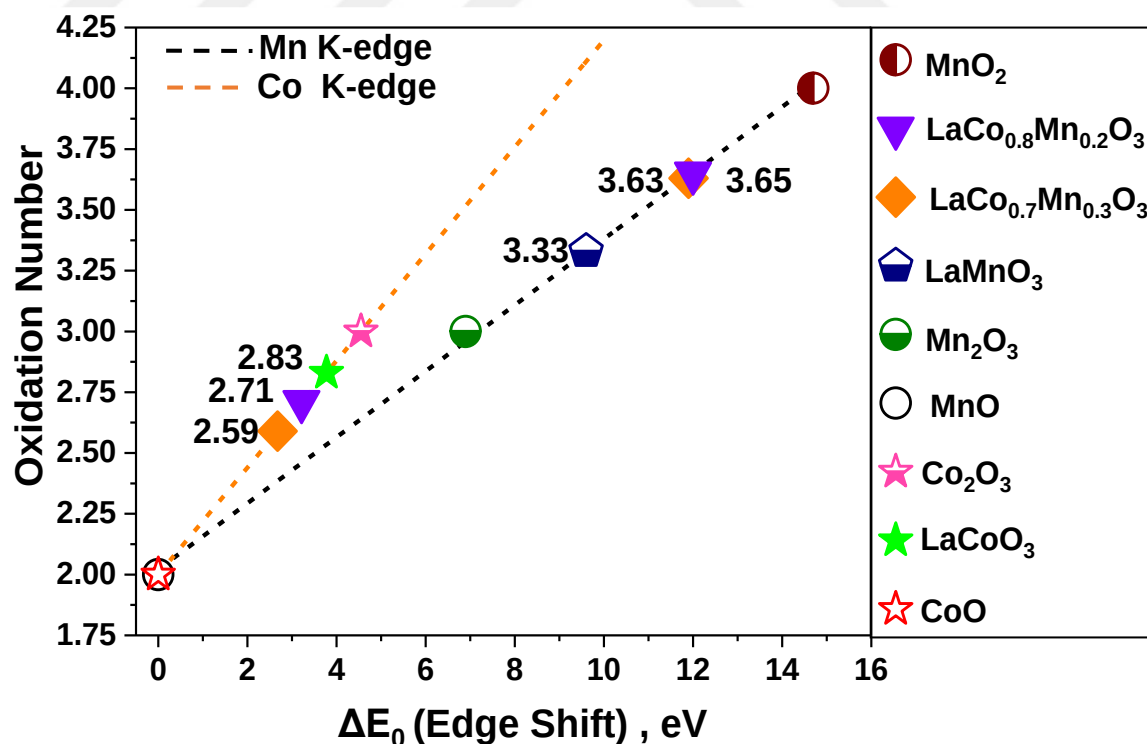


**Figure 4-9.** Average bulk oxidation states of Mn and Co as a function of  $\Delta E_0$  (Edge Energy Shift with respect to metal foil). Dashed (orange and black) lines represent linear fits obtained by the measurements of the reference samples with well-known oxidation states (i.e., Mn, MnO,  $\text{MnO}_2$  or Co, CoO,  $\text{Co}_2\text{O}_3$ ).

Shifts of Mn and Co K edges can be useful guides to follow the bulk oxidation state differences of B-site cations in simple and B-site mixed perovskites assuming that oxidation state varies as a linear function of the edge energy, which is verified by the linear behavior in the experimental data given in **Figure 4-9** [209]–[212]. **Figure 4-9** indicates that *average* bulk oxidation state of Mn in  $\text{LaMnO}_3$  is +3.33. It can be argued that  $\text{Mn}^{3+}$  is the prevalent bulk oxidation state in  $\text{LaMnO}_3$ , however presence of a smaller extent of  $\text{Mn}^{4+}$  state shifts the average bulk oxidation state to a value greater than +3 and renders the  $\text{LaMnO}_3$  bulk structure slightly richer in oxygen with respect to the conventional perovskite stoichiometry of  $\text{ABO}_3$ . This is also in line with the current XPS results suggesting the existence of  $\text{Mn}^{4+}$  states with a possible contribution from  $\text{Mn}^{3+}$  states on the surface of  $\text{LaMnO}_3$ . Thus, co-presence of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  states in  $\text{LaMnO}_3$  is conceivable both based on XPS and XANES results. Note that due to its relatively non-reducible nature, La has a persistent oxidation state of +3 in all of the analyzed samples verified by the current XANES measurements (**Figure 4-10**).

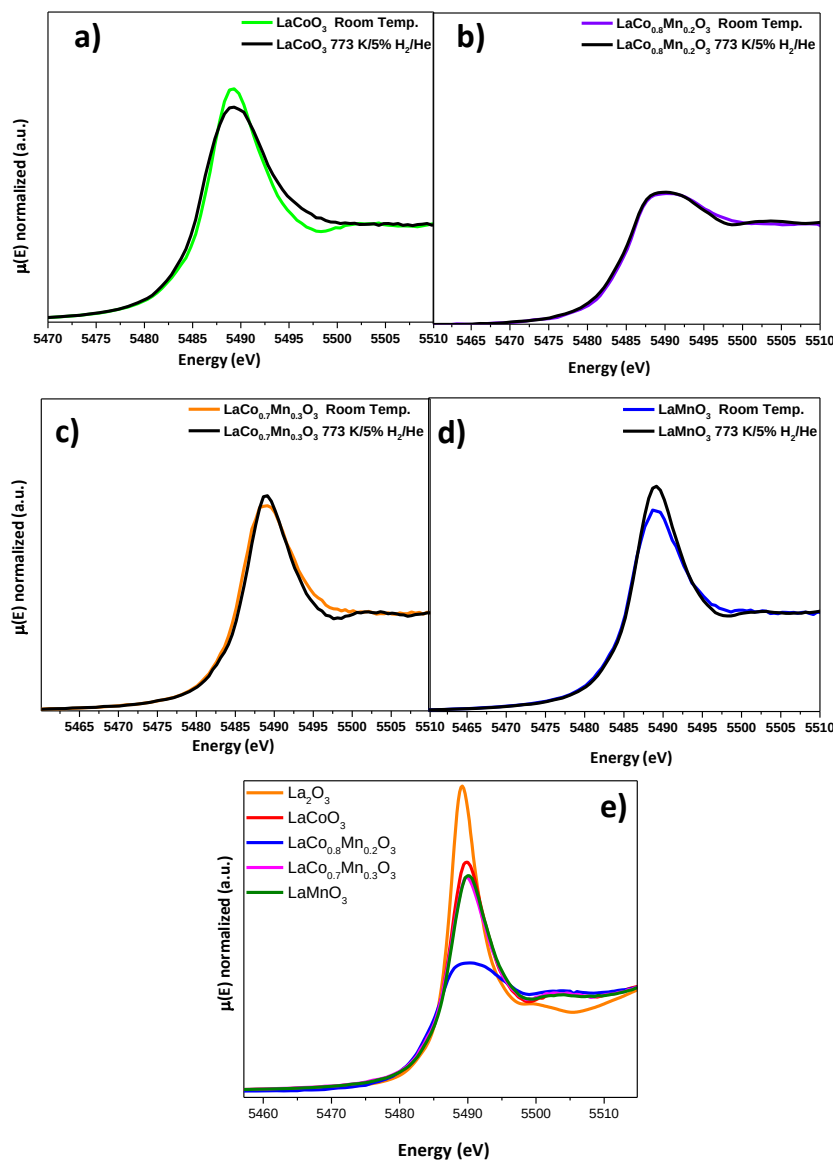


**Figure 4-10.** The comparison of La L-III edge for a)  $\text{LaCoO}_3$ , b)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , c)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and, d)  $\text{LaMnO}_3$  under reducing (773 K in the flow of 5%  $\text{H}_2/\text{He}$  mixture) and ambient conditions. e) Ex-situ XANES La L-III edge data for  $\text{La}_2\text{O}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ,  $\text{LaMnO}_3$ .

**Figure 4-10** illustrates the *ex-situ* XANES measurements of La L-III edge for  $\text{La}_2\text{O}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaMnO}_3$ . XANES spectra in **Figure 4-10a-10d** were taken at 773 K under the flow of 5%  $\text{H}_2/\text{He}$  gas mixture for  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaMnO}_3$ . While, **Figure 4-10e** shows data obtained at ambient conditions for  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaMnO}_3$  have additional data at 773 K in the 5%  $\text{H}_2/\text{He}$  mixture demonstrated in **Figure 4-10a-10d**. The main reason for performing La L-III XANES measurements was to show the invariance of the  $\text{La}^{3+}$  oxidation state in all of the investigated perovskite systems. The oxidation state

stability of La is extremely important to determine oxygen content of perovskites accurately by ICP-MS and *ex-situ* XANES results of B site cations. Hence, the invariance of La L-III edge as a function of reaction conditions is demonstrated in **Figure 4-10**. Similar La L-III edge energies of perovskites and La<sub>2</sub>O<sub>3</sub> confirms that there is no La oxidation state difference in these systems [213] (**Figure 4-10e**). First, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> XANES spectrum was taken in transmission mode where others were recorded in fluorescence mode to provide improved signal to noise ratio. Thus, the significant white line intensity (WLI) difference of LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> when compared to other perovskites could be explained via detection technique change. However, WLI differences between reference lanthanum oxide and perovskites might be correlated with filling level (number of DOS) of 5d orbitals of La atom. The earlier reports indicate that WLI can be changed by hydrogenation of metallic La without altering oxidation state [213], [214]. The crystallographic ordering of the lattice structure (*e.g.* atomic distances upon particle size and crystal structure changes [213]) or hydrogenation of La bonded oxygen atoms (hydroxide formation) may induce changes in WHL. Thus, exact origins of such changes are complex and relatively unknown for the currently investigated materials. However, despite the differences in WLI of given perovskites, all La-III edge positions are identical to the synthesized perovskites suggesting that they all have an identical La bulk oxidation state which is +3.

**Table 4-4.** Co K-edge and Mn K-edge energy ( $E_0$ ) values obtained from current *ex-situ* XANES measurements of the fresh perovskites and reference oxides.

| Co K-edge                                            | Edge Energy (eV) | Reference         |
|------------------------------------------------------|------------------|-------------------|
| LaCoO <sub>3</sub>                                   | 7723.3           | This work.        |
| LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub> | 7722.7           | This work.        |
| LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub> | 7722.1           | This work.        |
| CoO (Co <sup>2+</sup> )                              | 7719.5           | This work.        |
| Co <sup>3+</sup>                                     | 7724.0           | Literature value* |
| Mn K-edge                                            | Edge Energy (eV) | Reference         |
| LaMnO <sub>3</sub>                                   | 6553.2           | This work.        |
| LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub> | 6555.6           | This work.        |
| LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub> | 6555.5           | This work.        |
| MnO (Mn <sup>2+</sup> )                              | 6543.6           | This work.        |
| Mn <sub>2</sub> O <sub>3</sub> (Mn <sup>3+</sup> )   | 6550.5           | This work.        |
| MnO <sub>2</sub> (Mn <sup>4+</sup> )                 | 6558.3           | This work.        |

\* $E_0$  value for Co<sup>3+</sup> was verified from ref [208].

On the other hand, **Figure 4-9** shows that average bulk oxidation state of cobalt in  $\text{LaCoO}_3$  is +2.83, which is a clear indication of oxygen deficiency (note that the oxidation state of La is +3), as reported in the literature [214] and verified in the current work (see **Figure 4-10**). This observation is in good accordance with the current XPS results indicating a prevalent surface Co oxidation state of +3 with a minor contribution from +2 states on  $\text{LaCoO}_3$ .

Average bulk oxidation states of the B-site cations in the B-site mixed and simple perovskites are given in **Figure 4-9**. For the B-site mixed perovskites, these values were calculated by considering the relative metal abundances obtained from ICP-MS and multiplying each relative abundance value with the corresponding average bulk oxidation state of each cation determined *via* XANES. For instance, based on ICP-MS data (where total A and B site is normalized to 2.00), the B-site mixed perovskite formula can be expressed as  $\text{La}_x\text{Co}_y\text{Mn}_z\text{O}_{3+\alpha}$  and the average of each ion in the bulk can be written as  $\text{La}^{q_1}\text{Co}^{q_2}\text{Mn}^{q_3}\text{O}^{2-}$  (where  $q_1$ ,  $q_2$ ,  $q_3$  are the cationic charges in the bulk structure). By combining the mathematical relationships for bulk stoichiometric composition and that of the bulk average oxidation states, one can construct a charge conservation equation representing the electrical neutrality of the bulk perovskite structure as follows:

$$(x_{\text{La}} \times q_1) + (y_{\text{Mn}} \times q_2) + (z_{\text{Co}} \times q_3) = ((3 + \alpha)_{\text{O}^{2-}} \times (-2)) \quad 4-1$$

As it was mentioned before, ionic crystals should be electrically neutral in their macroscopic/bulk forms. In other words, total positive charge present in the crystal should be identical to the total negative charge (see equation (4-1)). Electrical-neutrality requirement could be used to estimate the bulk oxygen stoichiometry of the currently investigated perovskite structures. This can be done by combining the bulk composition information provided by ICP-MS data (**Figure 4-4**) and the average cation oxidation state information provided by the XANES results (**Figure 4-9**). By utilizing the relative bulk composition of each cation from ICP-MS data and the average bulk oxidation state of each ion from XANES data, one can estimate the total positive charge present in the formula unit of each perovskite originating from all A-site and B-site cations. Since the total positive cationic charge needs to be compensated by the  $\text{O}^{2-}$  anions in the structure to

satisfy the electrical neutrality of the unit cell, one can estimate the relative number of oxide ions that should be present in the perovskite formula unit (see **Table 4-5**).

In order to do this, we can start by assuming that the total number of cations (*i.e.*, A+B) in the perovskite formula unit is 2. This seems to be a reasonable assumption as a stoichiometric (ideal) perovskite has one A-site cation and one B-site cation per formula unit. Using this assumption, along with the relative number of cations present in the bulk structure provided by the ICP-MS data, relative number of cations in the formula unit can be calculated (**Table 4-3**).

In this fashion, relative number of La, Co, Mn cations determined experimentally by ICP-MS were multiplied with appropriate factors so that total number of cations in the perovskite formula unit is 2, while keeping the relative ICP-MS-based cation ratios constant. Then, by using these normalized cation compositions, we calculate the total positive (cationic) charge per formula unit by multiplying the normalized cation abundances with the average bulk oxidation states of each cation obtained by the current XANES measurements (**Figure 4-9**). Addition of these individually corrected cationic charges yields the total positive charge per formula unit due to all A and B-site cations. Using this total positive charge in the crystal, one can compute the number of bulk O<sup>2-</sup> anions required to satisfy the total positive charge in the formula unit and establish the electrical neutrality.

Once the oxygen stoichiometries of the investigated perovskites are determined, then they can be readily compared with an ideally stoichiometric perovskite, ABO<sub>3</sub>. Oxygen deficiency or surplus in the investigated perovskites is represented by the oxygen deficiency/surplus coefficient, “ $\alpha$ ”, given in **Table 4-5**. For an ideal perovskite,  $\alpha$  is equal to zero (*i.e.*,  $3 + \alpha = 3$ ), suggesting the lack of any oxygen deficiency or oxygen surplus. Results given in **Table 4-5** are in perfect agreement with literature suggesting that LaMnO<sub>3</sub> is surplus in oxygen, while LaCoO<sub>3</sub> is oxygen deficient [215], [216].

On the other hand, LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> reveal a unique bulk oxygen deficiency, which is in between two extreme cases presented by LaMnO<sub>3</sub> and LaCoO<sub>3</sub>.

Hence, bulk stoichiometry of the  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  systems were determined to be  $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{2.97}$  and  $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{2.97}$ .

These results suggest that bulk electronic properties of the B-site mixed perovskites can be fine-tuned using the current synthesis strategy to obtain uniquely different materials with unusual oxygen vacancy populations in the bulk. This unusual oxygen vacancy population could be one of the primary reasons for the superior redox reactivity of these B-site mixed materials as will be shown in the forthcoming sections.

It is important to mention that the above treatment assumes all of the La, Co, and Mn atoms in the *bulk* are in the perovskite structure and no other bulk phases are exist other than the perovskite structure. We believe that this is a reasonable assumption since: a) XRD data do not reveal any bulk crystalline phases other than perovskites, b) experimentally obtained ICP-MS elemental ratios are in very good agreement with the nominal perovskite stoichiometry predicted by the relative amounts of synthesis precursors used in the synthetic protocol. In other words, additional surface phases (that are different than perovskites) implied by the current XPS data correspond to only minority species which are much smaller in content as compared to the *bulk* perovskite phases.

**Table 4-5.** Estimation of the oxygen stoichiometry of the investigated perovskites by combining the current ex-situ XANES and ICP-MS results (see text for details).

| Sample Name                                           | Relative # of La atoms per formula unit | Relative # of Co (or Mn) atoms per formula unit | Total # of A & B Cations per formula unit | Average Oxidation State of A-site cation: La | Average Oxidation States of B-site cations: Co (Mn) | Total positive charge per formula unit | Relative # of $\text{O}^{2-}$ anions per formula unit required for electrical neutrality | Oxygen deficiency/surplus coefficient « $\alpha$ » |
|-------------------------------------------------------|-----------------------------------------|-------------------------------------------------|-------------------------------------------|----------------------------------------------|-----------------------------------------------------|----------------------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------|
| $\text{ABO}_{3+\alpha}$                               | 1.00                                    | 1.00                                            | 2.00                                      | +3                                           | +3.00                                               | +6                                     | 3.00                                                                                     | 0.00                                               |
| $\text{LaCoO}_{3+\alpha}$                             | 0.97                                    | 1.03 (N/A)                                      | 2.00                                      | +3                                           | +2.83 (N/A)                                         | +5.82                                  | 2.91                                                                                     | -0.09                                              |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_{3+\alpha}$ | 1.01                                    | 0.75 (0.24)                                     | 2.00                                      | +3                                           | +2.71 (+3.65)                                       | +5.94                                  | 2.97                                                                                     | -0.03                                              |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_{3+\alpha}$ | 1.04                                    | 0.65 (0.31)                                     | 2.00                                      | +3                                           | +2.59 (+3.63)                                       | +5.93                                  | 2.97                                                                                     | -0.03                                              |
| $\text{LaMnO}_{3+\alpha}$                             | 0.97                                    | N/A (1.03)                                      | 2.00                                      | +3                                           | N/A (+3.33)                                         | +6.34                                  | 3.17                                                                                     | +0.17                                              |

**Table 4-6.** Obtained EXAFS parameters for  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaMnO}_3$ .

| Sample/Main Absorber/Edge                                            | Scattering Type (SS, single scattering or MS, Multiple Scattering) | Path      | $N^a/\text{Degeneracy for MS}$ | $R \text{ (Å)}^b$ | $\sigma^2 (\times 10^{-3} \text{ Å}^2)^c$ | $\Delta E(\text{eV})^d$ |
|----------------------------------------------------------------------|--------------------------------------------------------------------|-----------|--------------------------------|-------------------|-------------------------------------------|-------------------------|
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | SS                                                                 | Co-O      | 6                              | $1.92 \pm 0.002$  | $2 \pm 0.2$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | SS                                                                 | Co-La     | 2                              | $3.28 \pm 0.01$   | $4 \pm 0.8$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | SS                                                                 | Co-La     | 6                              | $3.34 \pm 0.003$  | $4 \pm 0.3$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | SS                                                                 | Co-Co     | 6                              | $3.82 \pm 0.003$  | $7 \pm 0.8$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | MS                                                                 | Co-O-Co   | 12                             | $3.84 \pm 0.003$  | $7 \pm 0.4$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | MS                                                                 | Co-O-Co-O | 6                              | $3.86 \pm 0.005$  | $8 \pm 0.6$                               | $-1.74 \pm 0.2$         |
| $\text{LaCoO}_3/\text{Co}/\text{K edge}$                             | MS                                                                 | Co-O-O-O  | 6                              | $4.22 \pm 0.04$   | $12 \pm 0.7$                              | $-1.74 \pm 0.2$         |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-O      | 6                              | $1.94 \pm 0.003$  | $4 \pm 0.5$                               | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-La     | 2                              | $3.19 \pm 0.01$   | $3 \pm 1.1$                               | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-La     | 6                              | $3.33 \pm 0.003$  | $2 \pm 0.3$                               | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3/\text{Co}/\text{K edge}$ | MS                                                                 | Co-O-Co-O | 6                              | $3.72 \pm 0.4$    | $33 \pm 8.0$                              | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3/\text{Co}/\text{K edge}$ | MS                                                                 | Co-O-Co   | 12                             | $3.81 \pm 0.02$   | $29 \pm 4.0$                              | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-O      | 6                              | $1.95 \pm 0.01$   | $5 \pm 2.0$                               | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-La     | 6                              | $3.09 \pm 0.07$   | $14 \pm 12.0$                             | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-La     | 6                              | $3.31 \pm 0.02$   | $5 \pm 1.4$                               | $-2.35 \pm 0.2$         |
| $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{Co}/\text{K edge}$ | SS                                                                 | Co-Co     | 6                              | $4.00 \pm 0.03$   | $12 \pm 4.0$                              | $-2.35 \pm 0.2$         |
| $\text{LaMnO}_3/\text{Mn}/\text{K edge}$                             | SS                                                                 | Mn-O      | 6                              | $1.95 \pm 0.01$   | $7 \pm 0.8$                               | $-1.92 \pm 0.7$         |
| $\text{LaMnO}_3/\text{Mn}/\text{K edge}$                             | SS                                                                 | Mn-La     | 8                              | $3.38 \pm 0.01$   | $9 \pm 0.9$                               | $-1.92 \pm 0.7$         |
| $\text{LaMnO}_3/\text{Mn}/\text{K edge}$                             | SS                                                                 | Mn-Mn     | 6                              | $3.90 \pm 0.04$   | $18 \pm 6$                                | $-1.92 \pm 0.7$         |

<sup>a</sup> Degeneracy number (coordination number for single scattering path) for the given paths. <sup>b</sup> Distance between absorbing atom and atom in the corresponding shell. <sup>c</sup> Debye-Waller value. <sup>d</sup> The energy shift between fit and the experimental data.

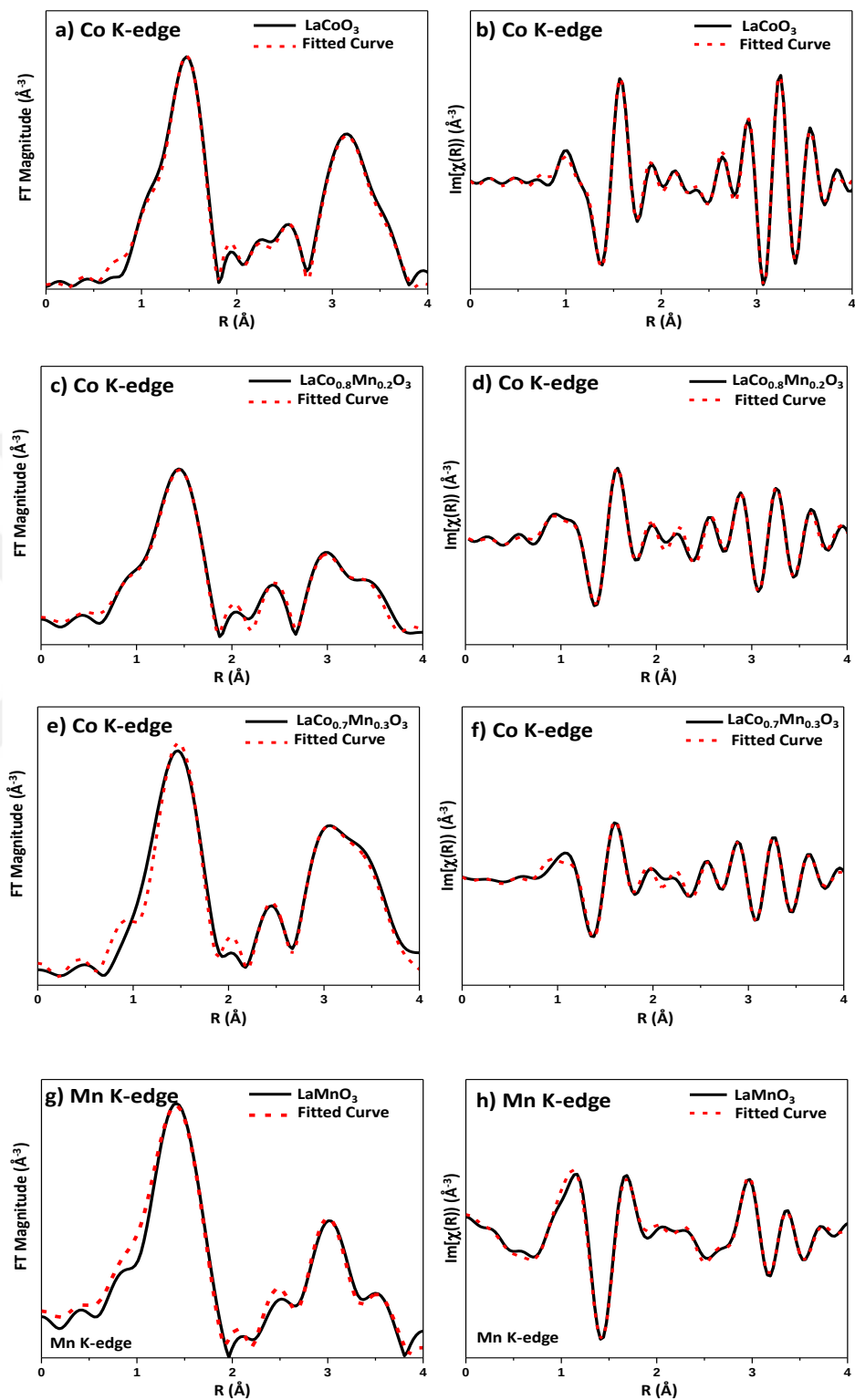


**Figure 4-11.** EXAFS results for a-b)  $\text{LaCoO}_3$ , c-d)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , e-f)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and g-h)  $\text{LaMnO}_3$ , where a), c), e) and g) panels indicate Fourier-Transform (FT) of  $k^2\chi(k)$  or simply  $\chi(R)$  and b), d), f), h) panels represent the Imaginary part of  $\chi(R)$  function ( $\text{Im}[\chi(R)]$ ).

Another crucial aspect is to identify the local environment of atoms in the perovskite structure as a function of Co and Mn loading. As mentioned above, information regarding the coordination of a given atom can be extracted from the EXAFS analysis. EXAFS experiments of simple and B-site mixed perovskites were conducted at DESY (Deutsches Elektronen-Synchrotron) in P65 beamline. Transmission mode was utilized to collect EXAFS region data where samples were spread on double-sided transparent Kapton tape. For Mn K-edge and Co K-edge the beam energies were aligned to 6539 eV and 7709 eV, respectively, where Mn and Co metallic foils were used for energy calibration. The extended structure was elongated to  $16 \text{ \AA}^{-1}$  at k-space for data acquisition. The data analysis was processed by using Demeter [181] software. In the analysis of EXAFS, each scattering path were determined by the FEFF calculations using the crystal structures of perovskites given in the corresponding PDF cards (*i.e.*, based on the XRD data in **Figure 4-1**). The coordination number for single scattering (SS) and degeneracy for multiple scattering (MS) were constrained based on the crystal structure information.

The **Table 4-6** and **Figure 4-11** point out the experimental EXAFS results and fitted curves for  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaMnO}_3$ . In the EXAFS model, 1<sup>st</sup> and 2<sup>nd</sup> coordination shells of each perovskite system were examined to indicate the local properties of the main absorber. A coordination number (CN) of 6 for the first shell of Co and Mn in all of the investigated perovskite seems are in very good accordance with the fitted curves, confirming that B-site cations coordinate to six  $\text{O}^{2-}$  ions. There two different Co-La distances for  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  samples given in **Table 4-6** which can be associated with the distortion in the perovskite crystal structure. On the other hand, in the second shell of all perovskite systems, La is the main contributor, where SS or MS of Co and/or Mn in the second shell may contribute only slightly (see **Figure 4-11** for evolved shoulders in the second shell). The fit parameters ( $R$  ( $\text{\AA}$ ),  $\sigma^2$ , and  $\Delta E$ ) given in **Table 4-6** for each perovskite are within the proper limits for accurate EXAFS modelling. Additionally, for  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  samples, it is not possible to distinguish the relative number of Mn and Co in the local environment of the main absorber. The atomic number of Mn and Co are 25 and 27, respectively. Hence as discussed in **Appendix C**, in order to have a measurable scattering difference form the neighboring

atoms, the atomic number difference between neighboring atoms should be at least 5. In general, it is seen that the EXAFS results are compatible with the crystal structures deduced by the XRD data. Some alterations in the crystal structure of the perovskite catalysts can be monitored by EXAFS results where a very limited increase in the bond lengths is observed in the first coordination shell as a function of increasing Mn loading into the  $\text{LaCoO}_3$  perovskite lattice.

#### **4.1.2. Monitoring Redox Properties of Perovskites under Oxidizing or Reducing Reaction Conditions via *In-situ* XANES and $\text{H}_2$ -TPR**

To demonstrate the functional differences due to variations in the perovskite structure, reduction and oxidation behavior of the synthesized perovskites were followed under reaction conditions *via in-situ* XANES by exposing the catalyst surfaces to  $\text{O}_2(\text{g})$  or  $\text{H}_2(\text{g})$  gas flow at a wide range of temperatures, where the alterations in the bulk oxidation states of the B-site cations were monitored.

In these experiments, each catalyst was initially pretreated at 393 K in  $\text{He}(\text{g})$  flow (50 ml/min) for 30 min. Then, the reducing gas flow (5 %  $\text{H}_2/\text{He}$ , 50 ml/min) was introduced over the catalyst and *in-situ* XANES spectra were recorded at 500, 600, 700 and 773 K during the temperature ramp. After the reduction at 773 K, sample was cooled down to room temperature (RT) in  $\text{He}(\text{g})$ . Then, the gas flow was switched to 10 %  $\text{O}_2/\text{He}$  (50 ml/min) for oxidation and regeneration at 500, 600, 700 and 773 K during the second temperature ramp.

**Figure 4-12** and **Figure 4-13** present the changes in the Co K-edge of the  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  catalysts for these series of experiments. For all samples, bulk reduction was discernable at  $T > 600$  K (**Figures 4-12a-c**). Major indications of additional reduction appeared at 700 K, regardless of the perovskite composition. However, extent of reduction at 773 K was sensitive to the perovskite structure, where Co-K edge positions shifted differently, and the maximum shift was observed for  $\text{LaCoO}_3$  suggesting the greatest extent of reduction. In other words, increasing Mn loading in the B-site mixed perovskite architecture suppressed the Co reduction tendency. This is in

perfect accordance with the XANES results given in **Figure 4-9** and XPS results in **Figure 4-6** suggesting that Mn incorporation already reduces the Co cations and decreases their tendency for further reduction under reaction conditions with H<sub>2</sub>.

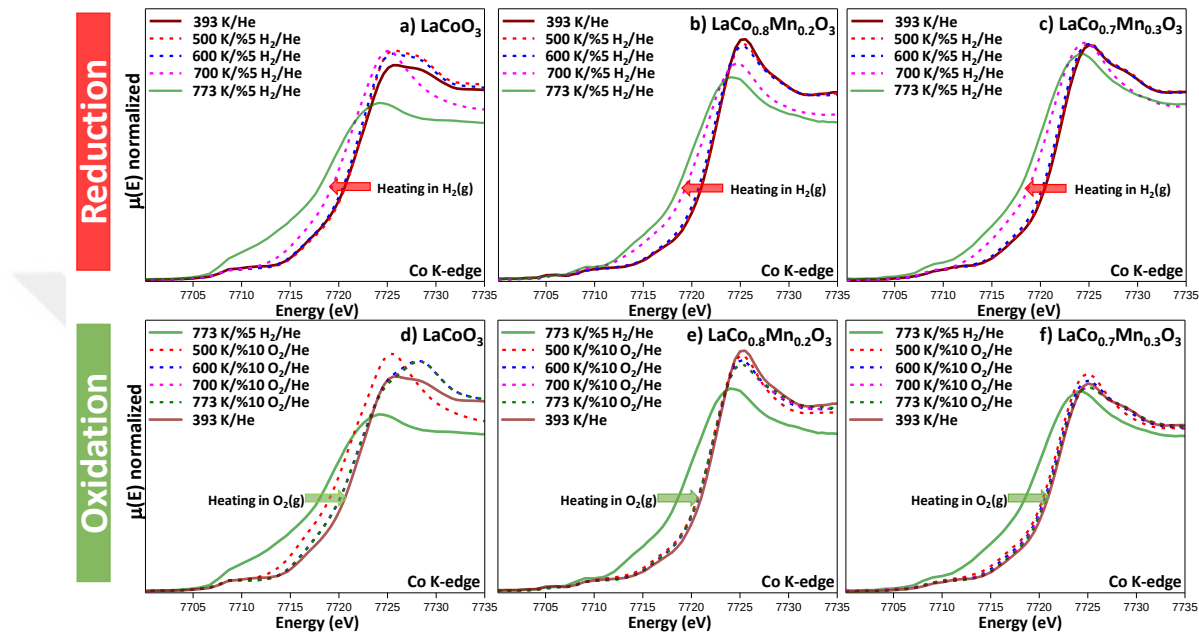
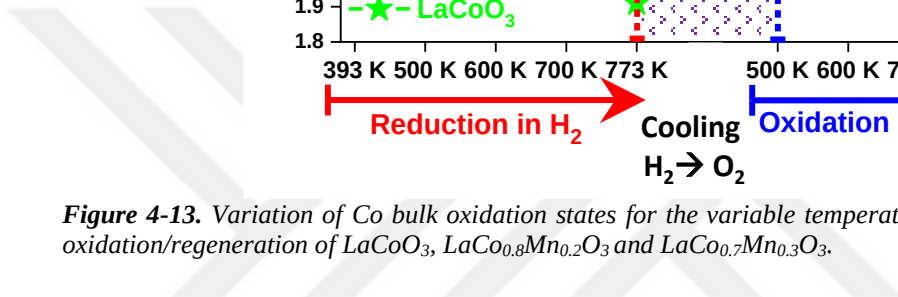


**Figure 4-12.** Co K-edge in-situ-XANES data for the variable temperature reduction and successive oxidation/regeneration of LaCoO<sub>3</sub>, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> and LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> in (a-c) 5 % H<sub>2</sub>/He (50 ml/min) and (d-f) 10 % O<sub>2</sub>/He (50 ml/min), respectively.

Co K-edge oxidation/regeneration behavior of the reduced samples shows interesting variations as a function of perovskite structure (**Figures 4-12d-f**). It was observed that due to their lesser extent of reduction (**Figures 4-12a-c**), B-site mixed perovskites can be readily regenerated at temperatures below 773 K, while LaCoO<sub>3</sub> required much higher temperatures for oxidative regeneration. This latter observation may be originating from the extensive phase segregation and sintering/growth of reduced Co sites in LaCoO<sub>3</sub>, whose existence was suppressed in the presence of Mn [217]. Thus, it is evident that Co cations in LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskites reveal a much more reversible redox behavior under reaction conditions within a low-temperature window of 400-500 K (where many catalytic oxidation/reduction reactions take place) as compared to that of LaCoO<sub>3</sub>, requiring higher temperatures (T > 700 K) for regeneration. A detailed view of the variations in the Co oxidation states during *in-situ* reduction and successive oxidation/regeneration experiments are provided in **Figure 4-12**.



— 393 K/He a) LaMnO<sub>3</sub> — 393 K/He b) LaCo<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>3</sub> — 393 K/He c) LaCo<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>3</sub>

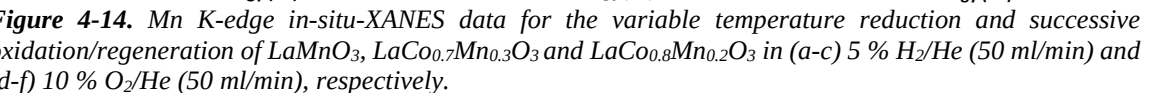


**Figure 4-14** and **Figure 4-15** represent the Mn-K edge data of the same series of reduction and successive oxidation/regeneration experiments. It is seen in **Figures 4-14a-c** that beginning of the reduction of Mn sites in  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  requires

relatively higher temperatures (*i.e.*, 700 K) as compared to that  $\text{LaMnO}_3$  which shows initial signs of reduction at temperatures as low as 600 K. On the other hand, B-site mixed perovskites showed a much more facile Mn regeneration/re-oxidation capability, where the reduced structure was fully regenerated at 500 K in  $\text{O}_2$ , while  $\text{LaMnO}_3$  was not fully regenerated even at 700 K in  $\text{O}_2$  (**Figures 4-14d-f**). Furthermore, **Figure 4-14** shows that ultimate Mn oxidation state change (Mn K-edge shift, see **Figure 4-14a**) during the reduction series is higher for  $\text{LaMnO}_3$  as compared to  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ .

Combining the results of **Figure 4-14** and **Figure 4-12**, it is evident that under mild/moderate reduction conditions studied above (**Figures 4-14a-c** and **Figures 4-12a-c**), maximum extent of reduction of the B-site cations can be ranked in the following order:  $\text{LaCoO}_3 > \text{LaMnO}_3 > \text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3 \approx \text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ . However, while reduced  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  require elevated temperatures for oxidative regeneration,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  can be readily regenerated at much lower temperatures (**Figures 4-14d-f** and **Figures 4-12d-f**). These trends are in very good agreement with a former study on NO oxidation, where  $\text{LaCoO}_3$  was found to be more active but less stable than  $\text{LaMnO}_3$ , possibly due to the irreversible redox behavior of  $\text{LaCoO}_3$  [32].

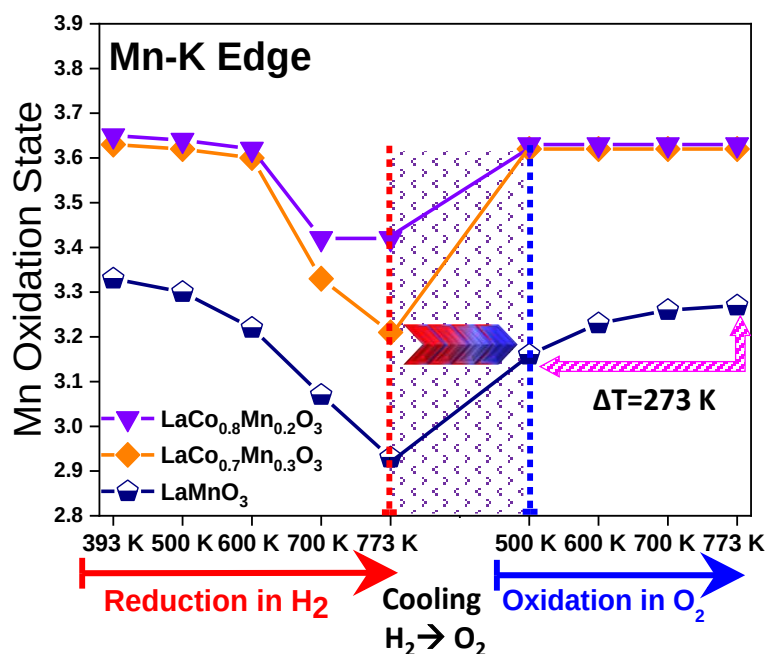


**Figure 4-15.** Variation of Mn bulk oxidation states for the variable temperature reduction and successive oxidation/regeneration of  $\text{LaMnO}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ .

For a catalyst to be efficient, it should first perform the catalytic reaction by converting the reactants. After the formation of the products, spent catalyst should rejuvenate itself and return to the original active state by regeneration. Likewise, a redox catalyst should first activate/convert reactants by electron transfer, then regenerate itself by reverse electron transfer, and complete the catalytic cycle. **Figure 4-14** and **Figure 4-12** indicate that B-site mixed perovskites show a higher efficiency in switching between oxidized and reduced states in the presence of  $H_2(g)$  and  $O_2(g)$  flow at low temperatures (*i.e.*, under mild/moderate redox environments) revealing their superior redox reversibility without the need for elevated temperatures.

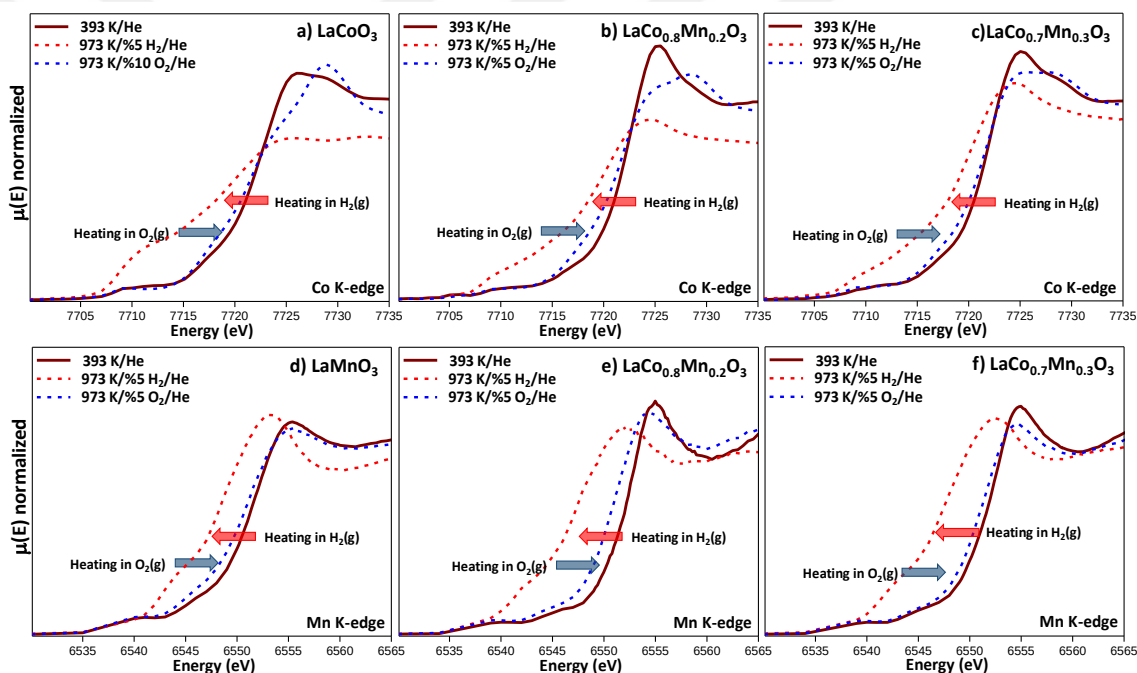


**Figure 4-16.** Co and Mn K-edge in-situ-XANES data for extreme reduction and oxidation of  $LaCoO_3$ ,  $LaCo_{0.8}Mn_{0.2}O_3$ ,  $LaCo_{0.7}Mn_{0.3}O_3$  and  $LaMnO_3$  at 973 K.

Reduction/oxidation reactions performed under extremely harsh conditions such as elevated temperatures may lead to irreversible structural transformations, which can result in catalyst aging and deactivation. To examine such conditions, we have also exposed the catalysts directly to a reducing gas flow ( $H_2/He$ ) at 973 K followed by an oxidizing gas flow at same temperature as shown in **Figures 4-16a-f**. Upon reduction at 973 K, Co sites in  $LaCoO_3$  were converted to a metallic-like state (**Figures 4-16a**), which cannot be fully regenerated even after harsh oxidation at 973 K. Extent of reduction for B-site mixed perovskites at 973 K is much less as compared to  $LaCoO_3$ , where Co sites do not reach a

metallic state in the former case. Furthermore, extent of oxidative regeneration at 973 K is enhanced by decreasing the Co-content in the perovskite (**Figures 4-16b** and **4-16c**). **Figure 4-16d** shows that Mn sites in LaMnO<sub>3</sub> are also severely reduced at 973 K under the reducing environment, though their extent of reduction is less than that of Co sites in LaCoO<sub>3</sub> (**Figure 4-16d**). As in the case of LaCoO<sub>3</sub>, LaMnO<sub>3</sub> also cannot be fully regenerated after oxidation at 973 K (**Figures 4-16a-d**). On the other hand, it is observed that regeneration of the Mn sites is more facile for LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> (**Figure 4-16f**) than that of LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> (**Figure 4-16e**). In overall, **Figure 4-16** suggests that among the investigated perovskite catalysts LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> has the highest tolerance to function reversibly under harsh redox conditions at elevated temperatures (973 K). Thus, current *in-situ* XANES results indicate that fine-tuning the structural properties of perovskites by designing B-site mixed architectures may also allow tuning the redox functionality and stability/reversibility of these systems.

H<sub>2</sub>-TPR experiments were also performed to show redox reversibility of B-site mixed and simple perovskites. The results shown in **Figure 4-17** as well as the associated integrated TPR signals presented in **Figure 4-17b** demonstrate that LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> are not only capable of being reduced at lower temperatures (*i.e.*, 614 and 635 K) than LaCoO<sub>3</sub> and LaMnO<sub>3</sub> (*i.e.*, 660 K) but these B-site mixed perovskites can also surpass simple perovskites in terms of the total number of reduced sites at these low temperatures (*i.e.*, integrated  $\delta$ -signal in **Figure 4-17b**). It is worth emphasizing that the temperature window (400-750 K) associated with the  $\delta$ -signal is particularly important as it overlaps with the relevant CO oxidation and NO oxidation catalytic reaction temperatures which will be explained in **Section 4.1.5**. Furthermore, B-site mixed perovskites either outperform or are comparable with the simple perovskites in terms of the total number of reduced sites for the entire temperature range (*i.e.*, integrated  $\delta + \gamma$  signals in **Figure 4-17b**). Therefore, current H<sub>2</sub>-TPR data suggest that ease of reducibility of B-sites of the perovskite structures within 400-750 K can be associated with their corresponding catalytic NO oxidation reactivity (**Section 4.1.5**).

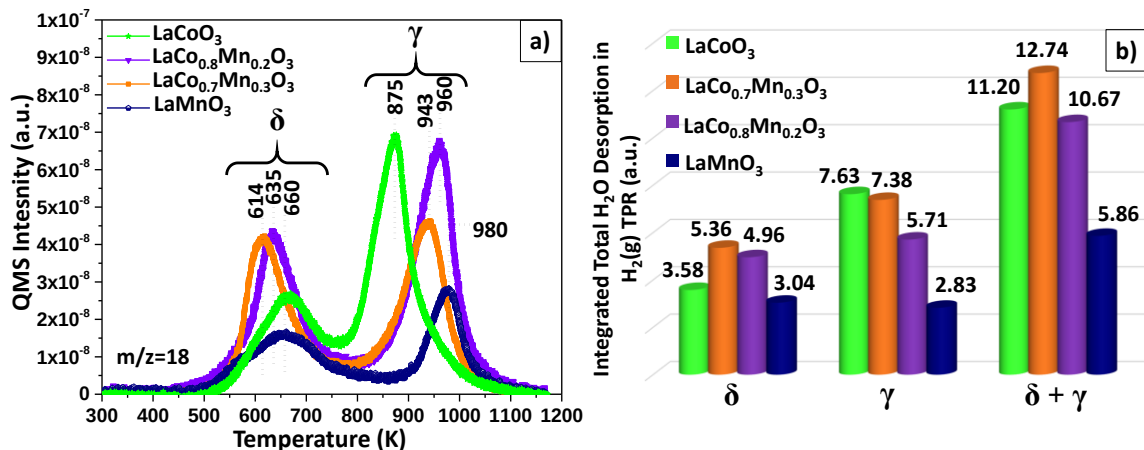
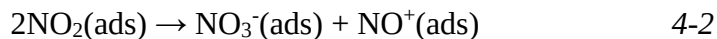


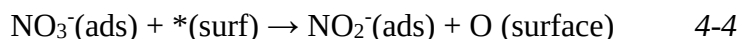
**Figure 4-17.** (a)  $\text{H}_2$ -TPR profiles, (b) integrated  $\text{H}_2\text{O}$  desorption signals in  $\text{H}_2$ -TPR data for  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ .

#### 4.1.3. Monitoring Catalytic $\text{NO}_2$ Disproportionation and $\text{NO}_x$ Storage via *In-situ* FTIR experiments

To demonstrate the relative reactivity of the investigated perovskite surfaces, we chose a catalytic storage process which has strong dependence on both surface and bulk defects. It is known that surface as well as bulk defects of reducible metal oxides play a crucial role in the catalytic  $\text{NO}_x$  storage. In other words,  $\text{NO}_x$  storage on reducible oxides is often not simply a passive sorption phenomenon but rather facilitated/catalyzed by surface sites. By performing XANES experiments and Density Functional Theory (DFT) calculations, Rodriguez *et al.* reported that adsorbed  $\text{NO}_2$  on  $\text{TiO}_2(110)$  revealed a synergistic interaction with the electronic states associated with oxygen vacancies which resulted in the diffusion of bulk oxygen vacancies to the surface and also stabilization of the surface oxygen vacancy sites [218]. In other words, it was shown that  $\text{NO}_2$  could be utilized as an excellent probe molecule not only to titrate surface oxygen vacancies but also bulk oxygen vacancies in an indirect manner. Thus, in the current work, we monitored catalytic  $\text{NO}_x$  storage via  $\text{NO}_2$  adsorption on perovskites using *in-situ* FTIR spectroscopy. It is well-known in the literature that  $\text{NO}_2$  storage on metal oxide surfaces often involves a disproportionation step, where  $\text{NO}_2$  is simultaneously oxidized and reduced to form surface nitrate and nitrosyl ( $\text{NO}$ )/nitrosonium reaction (4-2) [219]. This redox process can also be catalytically facilitated/assisted by the surface sites.



Furthermore, surface oxygen vacancies (\*) or surface oxide ions ( $\text{O}^{2-}(\text{surf})$ ) can be directly involved in  $\text{NO}_x$  storage through the following catalytic reactions (4-3) and (4-4):



To monitor above phenomena, the surfaces of fresh  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  catalysts saturated with  $\text{NO}_2(\text{g})$  at 323 K and the *in-situ* FTIR spectra were obtained for each catalyst (**Figures 4-17a-d**, blue spectra). As a comparison, we conducted similar  $\text{NO}_2(\text{g})$  adsorption and storage experiments on the same surfaces which were pre-reduced with  $\text{H}_2(\text{g})$  at 623 K (**Figures 4-18a-d**, red spectra). Pre-reduction temperature (*i.e.*, 623 K) was chosen in the light of the *in-situ* XANES experiments to avoid irreversible bulk reduction, while ensuring beginning of the reduction process for all of the investigated samples. Furthermore, this temperature is also a relevant choice for typical catalytic De $\text{NO}_x$  processes such as SCR and NSR coupled with a DOC. Identical experiments were also carried out for other  $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$  B-site mixed perovskites, where  $x = 0.1-0.9$ .

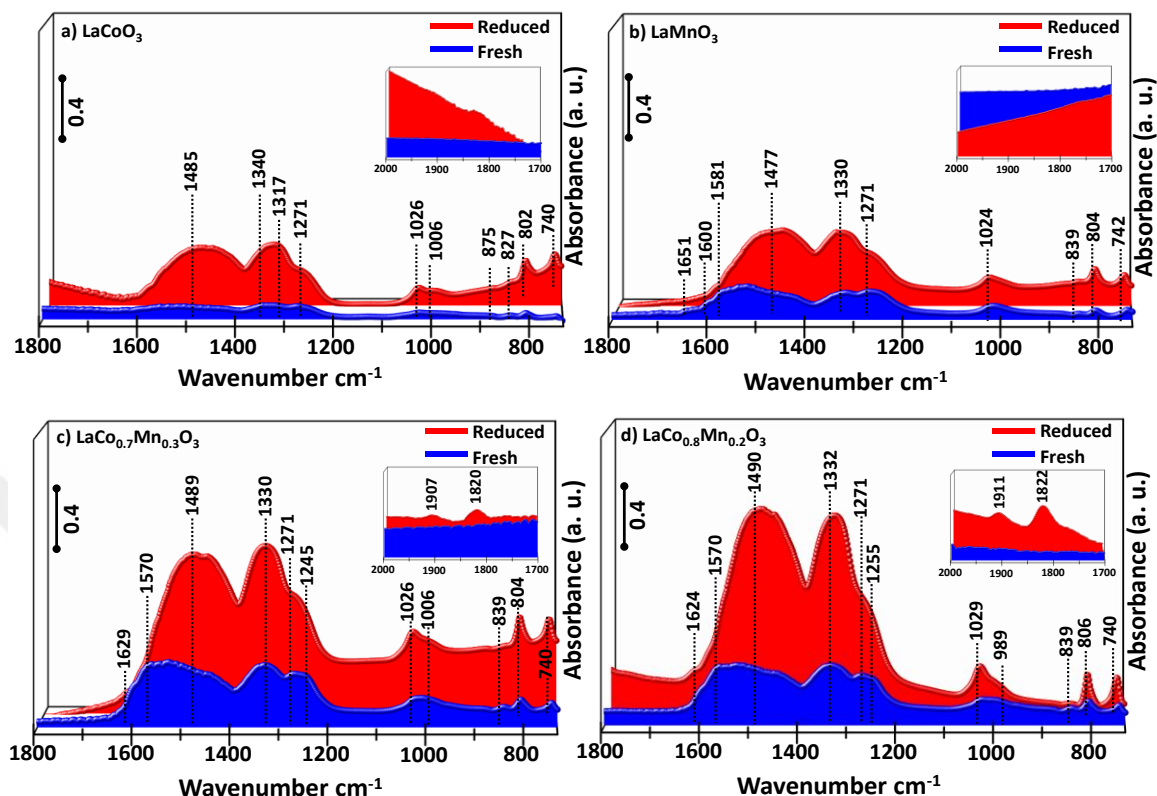


**Figure 4-18.** In-situ FTIR spectra for a)  $\text{LaCoO}_3$ , b)  $\text{LaMnO}_3$ , c)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and d)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  obtained after room temperature  $\text{NO}_2(\text{g})$  saturation of fresh (blue, bottommost spectra) samples, and samples reduced with  $\text{H}_2$  at 623 K (red/topmost spectra). All spectra were acquired at 323 K.

As can be seen in **Figure 4-18**, interaction of  $\text{NO}_2$  with perovskite surfaces led to the formation of various IR bands within  $700\text{--}1800\text{ cm}^{-1}$  which can be attributed to the formation of nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) species [144], [220]–[224]. **Figure 4-18**, IR bands at  $1629$  and  $1006\text{ cm}^{-1}$  can be assigned to the symmetric and asymmetric modes of bridging nitrates, respectively [220]. The signal at  $1629\text{ cm}^{-1}$  may be considered as the bending mode of  $\text{H}_2\text{O}$  which is doubtful at a given experimental conditions (*i.e.*, pretreated samples at 973 and high vacuum conditions). Bidentate nitrates were also visible at  $1570$  and  $1270\text{ cm}^{-1}$  [144], [221]. Furthermore, vibrational features within  $840\text{--}820\text{ cm}^{-1}$  ( $\nu_{\text{ONO}}$ , bending),  $1365\text{--}1075\text{ cm}^{-1}$  ( $\nu_{\text{N-O}}$ ) and  $1485\text{--}1400\text{ cm}^{-1}$  ( $\nu_{\text{N=O}}$ ) can be associated to nitrito species [222]–[225]. In addition, insets given in **Figures 4-18b** and **18c** indicate the formation of two additional weaker IR bands located at  $1911$  and  $1822\text{ cm}^{-1}$  that can be attributed to dinitrosyl species on  $\text{Co}^{2+}$  [226]–[228]. Formation of dinitrosyls point out that catalytic  $\text{NO}_2$  reduction to  $\text{NO}$  can be drastically boosted on  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  B-site mixed perovskites as a result of enhanced surface oxygen vacancy

generation on these latter surfaces. Additionally, nitrosyl signals can be assumed as overtones of N-containing species present on both simple and B-site mixed perovskites but lack of the IR (nitrosyl) signals on simple perovskites eliminates the possibility of combination signals.

Particularly, *in-situ* FTIR data given in **Figure 4-18** have four significant aspects that may allow us to identify important structure-functionality relationships which can correlate electronic structure and oxygen vacancies of perovskites with their reactivity. Firstly, for all cases, NO<sub>2</sub>(g) adsorption experiments performed under identical conditions revealed much higher NO<sub>x</sub>-related IR absorption intensities for B-site mixed perovskites as opposed to LaCoO<sub>3</sub> and LaMnO<sub>3</sub>. This observation suggests that unique electronic properties of LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> can catalytically activate NO<sub>2</sub> much better than that of LaCoO<sub>3</sub> and LaMnO<sub>3</sub> and facilitate NO<sub>x</sub>-storage. Note that this observation cannot be simply explained in the light of the SSA values of the catalysts (**Figure 4-3**). Even though, LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> had about 30 % lower SSA than that of LaMnO<sub>3</sub>, B-site mixed perovskites still revealed greater NO<sub>x</sub> storage. Comparing the SSA normalized NO<sub>x</sub> oxidation and storage capabilities of LaMnO<sub>3</sub> and LaCoO<sub>3</sub> (comparing **Figure 4-3** and **Figure 4-18**) suggests that LaCoO<sub>3</sub> is more efficient in NO<sub>x</sub> oxidation and storage per site basis. This can be attributed to the relatively higher oxygen vacancy population found in LaCoO<sub>3</sub>. On the other hand, LaCoO<sub>3</sub> suffers from low SSA. In contrast, LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskites reveal high SSA (**Figure 4-3**), high Co-content and moderately high bulk oxygen vacancy population (**Table 4-5**), optimizing the NO<sub>x</sub> oxidation and storage capability (**Figure 4-18**).

Secondly, as it can be seen in **Figure 4-18** that reduction with H<sub>2</sub> led to a discernible tilt in the baseline of the *in-situ* FTIR spectra which is an indication of a significant alteration in the electronic structure of the perovskites. This is to the formation of oxygen vacancies and alterations in the B-site oxidation states resulting in changes in the dielectric function of the materials and their wavelength-dependent IR absorption cross-sections. Tilting of the IR baseline has also been reported for reduced LaCoO<sub>3</sub> and LaMnO<sub>3</sub> in previous studies [21], [185]. It should be noted that this reduction-induced tilting in the IR spectra was reversible and could be removed by re-oxidizing the materials and healing/titrating the

defects and re-oxidation of B-site cations. Thirdly, reduction with H<sub>2</sub> resulted in a massive increase in catalytic NO<sub>x</sub> storage for all samples, where reduced LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskites revealed significantly greater NO<sub>x</sub>-related IR bands than all others. This observation is also in very good agreement with the presence of a higher concentration of oxygen vacancies on reduced B-site mixed perovskites which became accessible by adsorbed NO<sub>x</sub> species, stabilizing stored NO<sub>x</sub> species and increasing their surface coverage through reactions (4-2), (4-3), and (4-5). Finally, reduced LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskites revealed the nitrosyl (NO) features at *ca.* 1822 and 1911 cm<sup>-1</sup>. This suggests that the presence of a high concentration of vacancies on these surfaces could facilitate catalytic NO<sub>2</sub> storage *via* (4-4). It is important to mention that oxygen vacancy-assisted NO<sub>x</sub> storage on perovskites is a catalytic process, as these surfaces can be reversibly regenerated by subsequent reduction-oxidation cycles demonstrated by the current *in-situ* XANES experiments (**Figure 4-14** and **Figure 4-12**).

*In-situ* FTIR experiments qualitatively verified the greater affinity of the LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub> and LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskites for NO<sub>x</sub> storage. However, these experiments were not quantitative in nature due to the differences in the IR absorption cross sections of different NO<sub>x</sub> species precluding a direct correlation between IR intensities and surface concentrations. Hence, TPD experiments were performed in order to quantify reactivity and NO<sub>x</sub> storage differences.

**Figure 4-19** and **Figure 4-20** show the results of the TPD experiments which were performed immediately after each NO<sub>x</sub> storage experiment given in **Figure 4-18**. In these experiments, the following desorption channels were monitored: *m/z*=30, 44, 46 and 28, which corresponded to NO, N<sub>2</sub>O, NO<sub>2</sub>, and N<sub>2</sub>, respectively. It should be mentioned that *m/z* = 28 and 44 desorption channels probably had only minor contributions from CO and CO<sub>2</sub>. It is likely that these species were mostly removed from the surface before the TPD runs because of the oxidative cleaning pre-treatment as well as the additional high temperature annealing carried out at 973 K in vacuum.

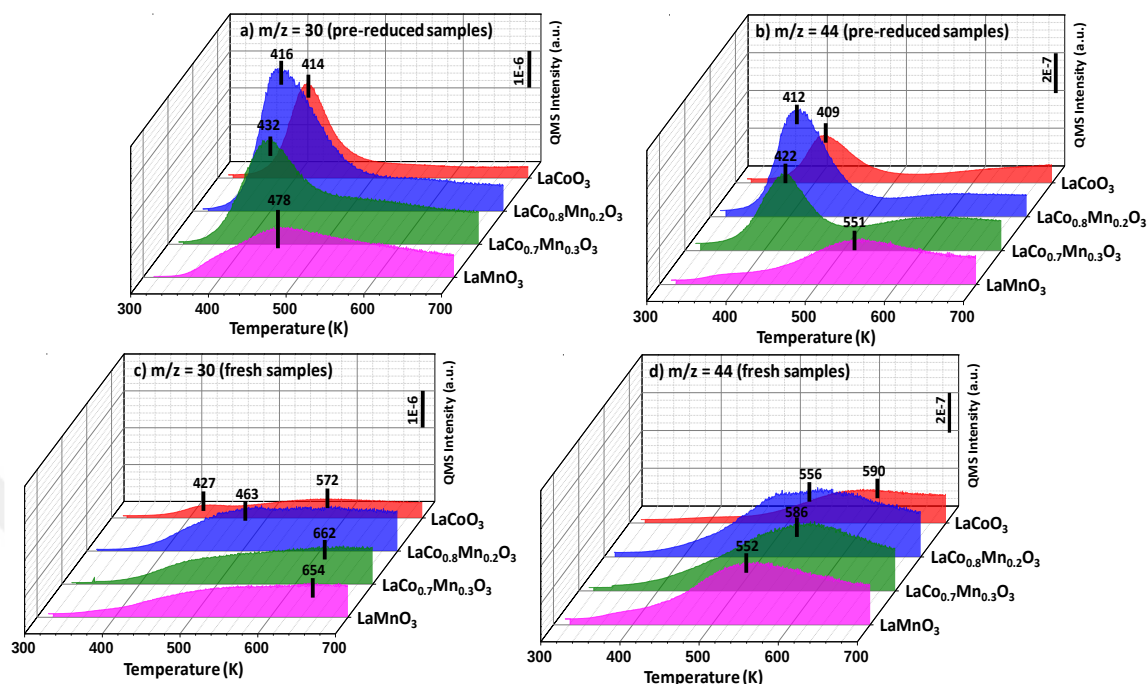
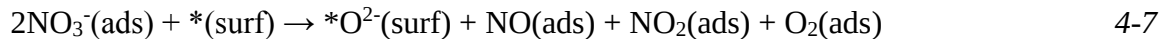
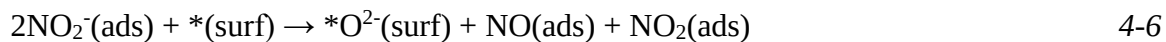


**Figure 4-19.** Selected TPD desorption channels obtained after  $\text{NO}_2$  saturation of investigated perovskites at 323 K. (a)  $m/z=30$  (NO) and (b)  $m/z=44$  ( $\text{N}_2\text{O}$ ) belong to samples reduced with  $\text{H}_2$  at 623 K; (c)  $m/z=30$  (NO) fresh, and d)  $m/z=44$  ( $\text{N}_2\text{O}$ ) belong to fresh samples. Note that the scale bars given in panels (a) and (c) are 5 times greater than that of panels (b) and (d).

**Figure 4-19** shows that for all samples, reduction with  $\text{H}_2$  increased the NO and  $\text{N}_2\text{O}$  desorption signal intensities as compared to that of the fresh samples. Furthermore,  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  yielded greater NO and  $\text{N}_2\text{O}$  desorption signals that also appeared at lower temperatures. These observations suggest that  $\text{NO}_x$  storage on B-site mixed perovskites, in the form of nitrates and nitrites, is greater than that of  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$ . The thermal catalytic decomposition of stored nitrates and nitrites can be accomplished at lower temperatures, which suggest lower catalytic activation barriers of decomposition/desorption for the B-site mixed perovskites. A similar argument holds for  $\text{N}_2$  desorption channels given in **Figure 4-20b** and **Figure 4-20d**, where B-site mixed perovskites revealed greater  $\text{N}_2$  desorption intensities and reduced samples surpassed the fresh samples in terms of their greater  $\text{N}_2$  desorption intensities and lower  $\text{N}_2$  desorption temperatures.

Particularly,  $\text{N}_2\text{O}$  and  $\text{N}_2$  desorption may deserve additional attention as formation of these desorption products requires catalytic activation of strong N-O or N=O bonds and generation of atomic N(ads) and O(ads) species on the surfaces. Furthermore, stored

nitrites and nitrates can also titrate/heal oxygen vacancies on the surfaces of perovskites during their decomposition/desorption through the following possible reactions:



An exception to the trends discussed above is observed for the  $\text{NO}_2$  desorption channels shown in **Figures 4-20a** and **20c**, where  $\text{NO}_2$  desorption amount is the highest for  $\text{LaMnO}_3$ , which is the perovskite with the highest SSA (**Figure 4-3**). It is likely that this could be due to the fact that a significant portion (though not all) of the  $\text{NO}_2$  desorption channel may originate from reversible/molecular/non-dissociate adsorption of  $\text{NO}_2$  reaction (**4-12**) with a smaller contribution from dissociative desorption pathways such as reactions (**4-6**) and (**4-7**). Therefore, it is possible that majority of the  $\text{NO}_2$  desorption from  $\text{LaMnO}_3$  is due to the reversible molecular adsorption process, which is predominantly dictated by the available number of surface adsorption sites and SSA.

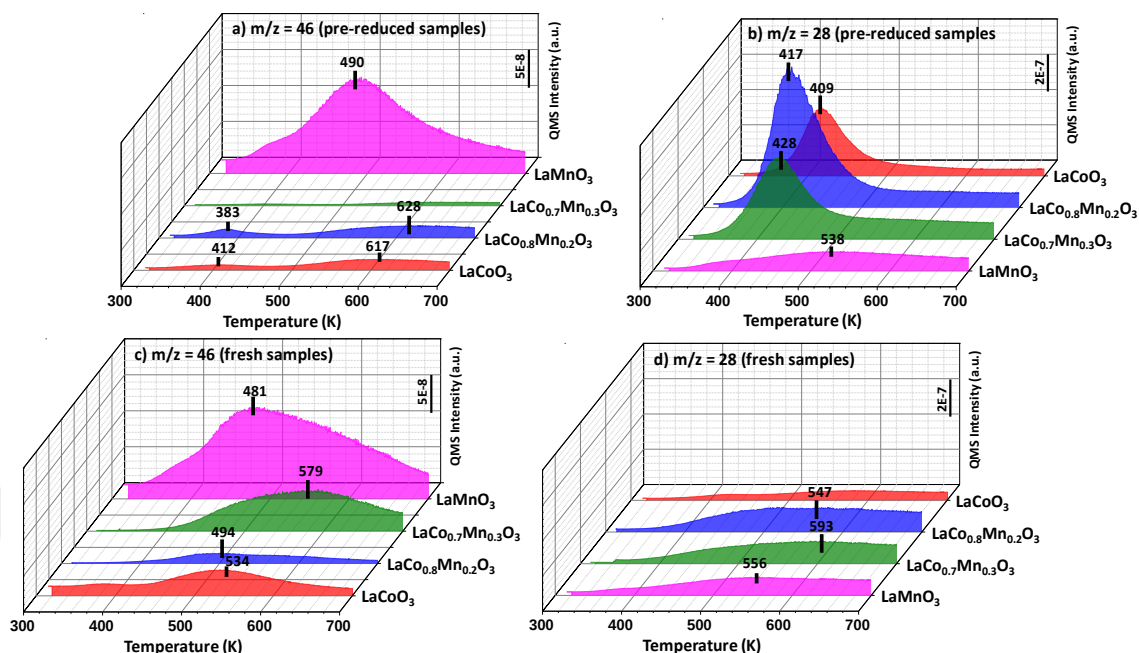


**Figure 4-20.** Selected TPD desorption channels obtained after  $\text{NO}_2$  saturation of investigated perovskites at 323 K. (a)  $m/z = 46$  ( $\text{NO}_2$ ) and (b)  $m/z = 28$  ( $\text{N}_2$ ) belong to samples reduced with  $\text{H}_2$  at 623 K; (c)  $m/z = 46$  ( $\text{NO}_2$ ) and (d)  $m/z = 28$  ( $\text{N}_2$ ) belong to fresh samples. Note that the scale bars given in panels (b) and (d) are 5 times greater than that of panels (a) and (c).

Clearly, the quantification of the stored/desorbing  $\text{NO}_x$  species cannot be achieved by directly comparing raw TPD desorption intensities given in **Figure 4-19** and **Figure 4-20**. Because  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  have overlapping mass spectroscopic fragmentation patterns, precluding direct intensity comparisons. Therefore, as explained in the **Section 3.15**, using mass spectroscopic fragmentation coefficients of all of the desorbing  $\text{NO}_x$  species (*i.e.*,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ), we calculated relative QMS intensities of all desorbing species in a quantitative fashion on all reduced (**Figure 4-21a**) and fresh samples (**Figure 4-21b**), in addition to the total relative number of stored  $\text{NO}_x$  species (*i.e.*, sum of corrected  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  TPD signals, **Figure 4-21c**). It is obvious that reduced  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  B-site mixed perovskites showed superior  $\text{NO}_x$  storage performance among all other fresh/reduced perovskites (see **Appendix A4**). Furthermore, these two reduced B-site mixed perovskites revealed the greatest amount of  $\text{NO}$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  desorption which required catalytic activation and bond scission in the stored nitrites reaction (4-6), nitrates reaction (4-7) and  $\text{NO}_2$  reaction (4-8). These observations also support the higher number of accessible/active oxygen vacancies that can be generated

on/in  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  B-site mixed perovskites *via* reduction by  $\text{H}_2$  at a moderate temperature of 623 K.

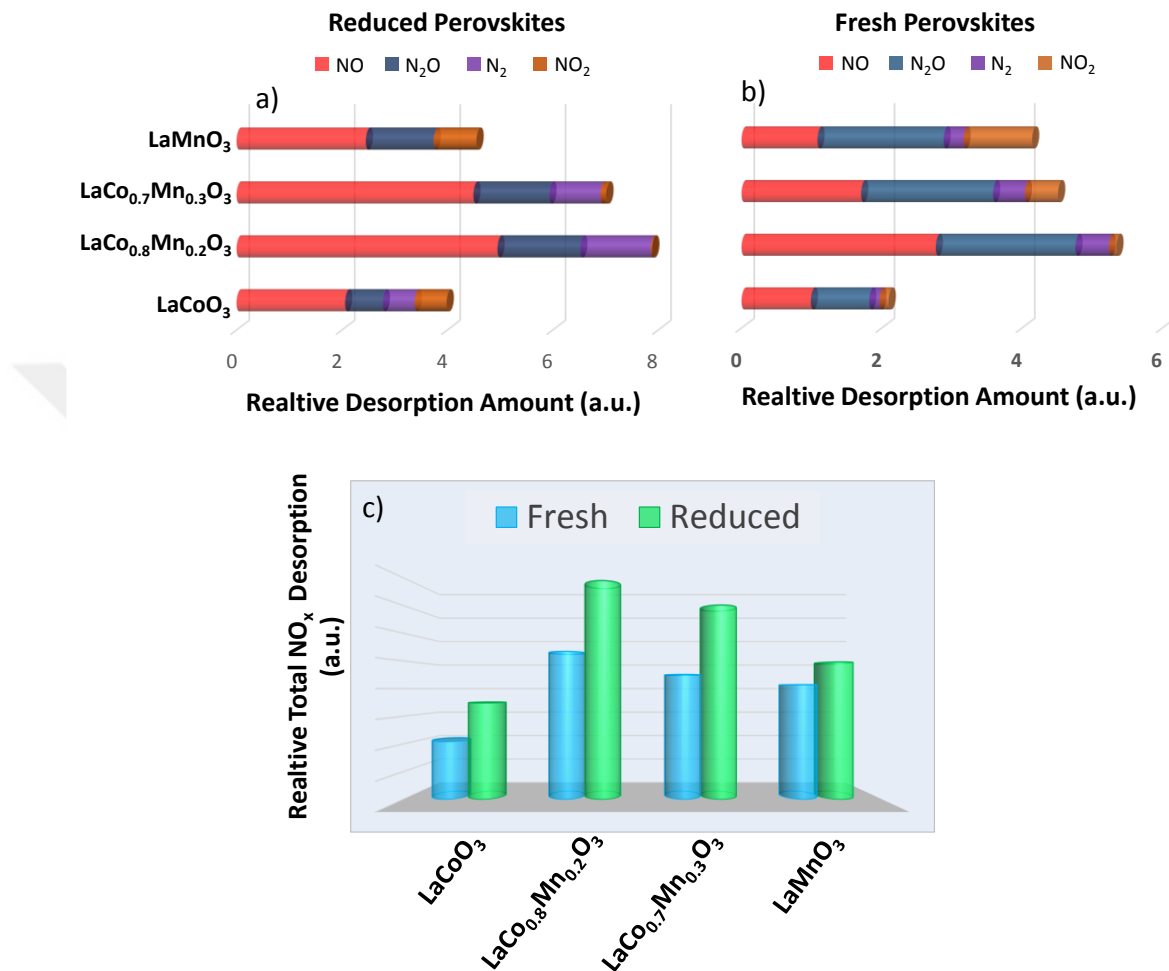


**Figure 4-21.** Quantification of the relative QMS intensities of all of the desorbing  $\text{NO}_x$  species calculated using mass spectroscopic fragmentation coefficients of  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  in TPD for (a) reduced and (b) fresh samples. (c) Relative total number of stored  $\text{NO}_x$  species (i.e., sum of corrected  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  TPD signals), obtained from panels (a) and (b).

**Figure 4-22** presents  $\text{H}_2\text{O}$  ( $m/z=18$ ) desorption channels acquired during the TPD experiments given in **Figure 4-19** and **Figure 4-20**. Since all perovskites were initially annealed at 973 K in vacuum inside the TPD chamber prior to  $\text{NO}_2$  adsorption and subsequent TPD runs, it is unlikely that water desorption signals in **Figure 4-22** originate solely from adsorbed molecular water. Presumably, they originate from dehydroxylation of the perovskite surfaces. It is seen that water desorption from  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  is significantly greater than that of  $\text{LaMnO}_3$  and  $\text{LaCoO}_3$ . Furthermore, reduction with  $\text{H}_2$  significantly boosts  $\text{H}_2\text{O}$  desorption on B-site mixed perovskites, while

reduction does not lead to a significant influence on water desorption for  $\text{LaMnO}_3$  and  $\text{LaCoO}_3$ . These results can be explained by the oxygen vacancy-assisted activation of  $\text{H}_2$  and formation of surface hydroxide/hydroxyl functionalities on reduced B-site mixed perovskites and recombinative desorption of surface hydroxide/hydroxyl species to form water as given in the following reactions (4-16), (4-17), (4-18) and (4-19).

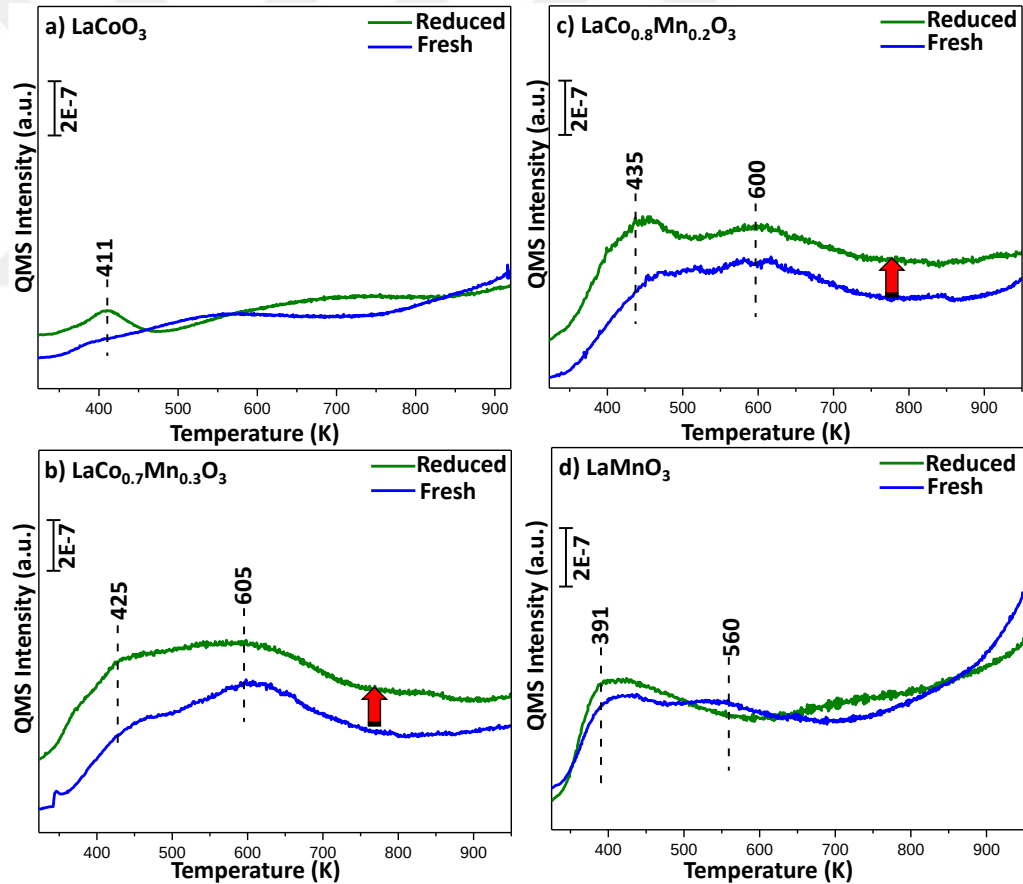
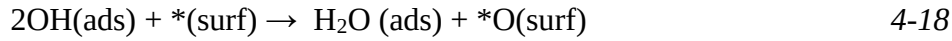
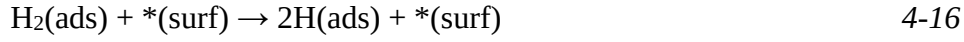


**Figure 4-22.**  $\text{H}_2\text{O}$  ( $m/z=18$ ) release of reduced (green line) and fresh (blue line) perovskites (a)  $\text{LaCoO}_3$ , b)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , c)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  and d)  $\text{LaMnO}_3$ .

#### 4.1.4. Monitoring Oxygen Vacancy Formation as a Function of Reduction Temperature on Model LaMnO<sub>3</sub> Perovskite Catalyst

*This section is reprinted (adapted) with permission of (Y. Sahin, A. T. Sika-Nartey, K. E. Ercan, Y. Koçak, S. Şenol, E. Ozensoy, Y. E. Türkmen “Precious Metal-Free LaMnO<sub>3</sub> Perovskite Catalyst with an Optimized Nanostructure for Aerobic C-H Bond Activation Reactions: Alkylarene Oxidation and Naphthol Dimerization,” ACS Applied Materials & Interfaces, 2021 (13) 5099-5110). Copyright (2022) American Chemical Society.*

While formation of dinitrosyls upon NO<sub>2</sub> reduction is quite useful to demonstrate oxygen vacancy formation on the perovskite surface (see **section 4.1.3**), it cannot provide unambiguous information about the relative concentration of oxygen vacancies and formation of superoxo (O<sub>2</sub><sup>-</sup>) and/or peroxo (O<sup>-</sup>) species that play a very significant role in the catalytic activity of perovskite catalysts. As it will be discussed in the forthcoming sections, type of activated oxygen species after reduction is critical especially for oxidation of CO (where LH mechanism is the dominant pathway) at low temperatures (see **section 4.1.5**). It is important to note that LaMnO<sub>3</sub> was chosen as a model catalyst to indicate formation of oxygen vacancy assisted activated oxygen species. Along these lines, we utilized O<sub>2</sub> as a probe molecule in the current in situ FTIR spectroscopic studies, where we investigated low-temperature (150 K) O<sub>2</sub>(g) adsorption on the perovskite catalysts. It is known that low-temperature adsorption of O<sub>2</sub> on reducible metal oxides may result in a unique vibrational signature around 1150 cm<sup>-1</sup>, which is due to the formation of metastable superoxide (O<sub>2</sub><sup>-</sup>(ads)) surface species [229]. Therefore, relative intensities of the O<sub>2</sub><sup>-</sup>(ads) vibrational features generated upon low-temperature O<sub>2</sub> adsorption can be exploited to compare relative surface oxygen vacancy concentrations on different reducible oxides. In light of this valuable information, *in-situ* FTIR spectra shown in **Figure 4-23** clearly suggest that increasing reduction temperature within 673–873 K monotonically increases the formation of surface oxygen vacancies on the reduced LaMnO<sub>3</sub> surfaces. However, upon extreme reduction at 973 and 1073 K, decomposition of the perovskite structure results in the formation of lower total surface oxygen vacancy concentration than that of 873 K (just before the second/harsh reduction of LaMnO<sub>3</sub>, see **Figure 4-17a**). This important experiment points to the fact that surface oxygen defect density on the perovskite surface is highly sensitive to the reduction temperature.

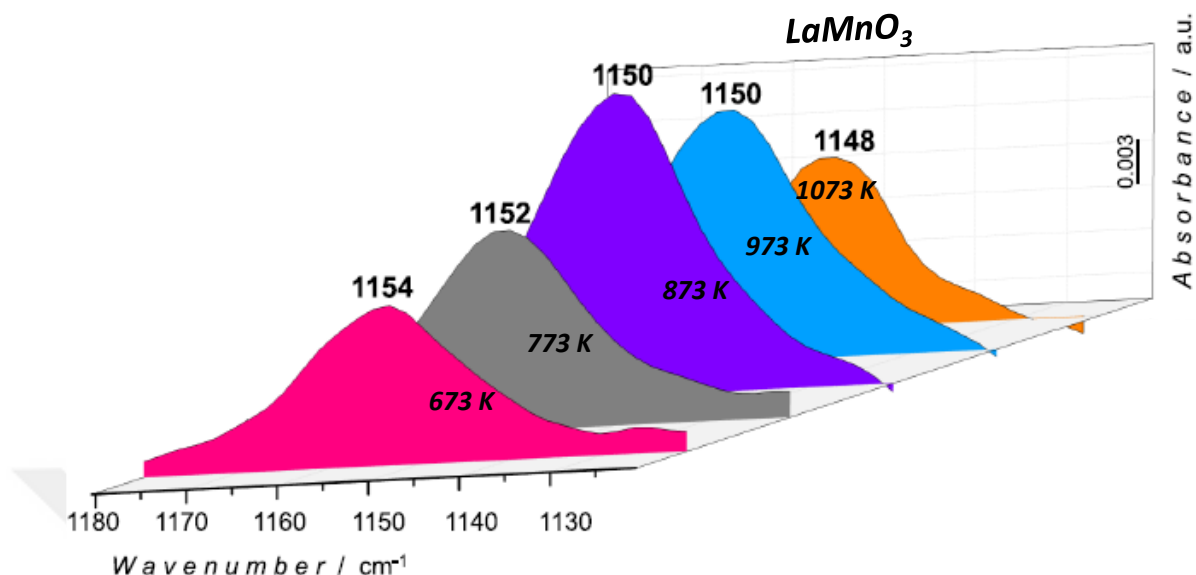


**Figure 4-23.** In-situ FTIR spectra for low-temperature (150 K)  $O_2$  adsorption on  $LaMnO_3$  catalyst pre-reduced at various temperatures.

#### 4.1.5. Flow Mode Catalytic NO Oxidation and CO Oxidation Tests and Long-Term Catalytic Stability Experiments on Single B-site and B-site Mixed Perovskites

As discussed in the previous sections, based on the *ex-situ*, *in-situ* characterization,  $NO_x$  adsorption/desorption experiments on fresh and  $SO_x$  poisoned samples, it was found out that Mn addition to  $LaCoO_3$  to obtain B-site mixed perovskites yielded enhanced surface chemical, electronic, and structural properties which may also result in a boost in catalytic performance and stability. Thus,  $LaCo_{0.8}Mn_{0.2}O_3$  and  $LaCo_{0.7}Mn_{0.3}O_3$  was chosen as the catalysts for flow mode catalytic performance tests, and  $LaCoO_3$  and  $LaMnO_3$  were used as benchmark catalysts to screen the effect of B-site mixing. Furthermore, 1% Pt/ $Al_2O_3$  was used as a conventional PGM benchmark catalyst to demonstrate the relative performance of B-site mixed perovskite catalysts as opposed to conventional precious metal catalysts used in commercial catalytic applications.

**Figure 4-24a** presents catalytic NO oxidation results for the investigated catalysts. These results indicate that the NO oxidation performances of these catalysts increase in the following order: 1 wt. % Pt/ $Al_2O_3$  <  $LaMnO_3$  <  $LaCoO_3$  <  $LaCo_{0.7}Mn_{0.3}O_3$  <  $LaCo_{0.8}Mn_{0.2}O_3$  clearly demonstrating the superior NO oxidation performance of B-site mixed perovskites

surpassing the PGM benchmark catalyst (1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>) and simple (LaCoO<sub>3</sub> and LaMnO<sub>3</sub>) perovskites. **Figure 4-24b** depicts the catalytic CO oxidation activity of the optimized La<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>3+α</sub> (B-site mixed) perovskites as compared to LaCoO<sub>3</sub>, LaMnO<sub>3</sub> (simple) perovskites, and the 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark PGM catalyst.

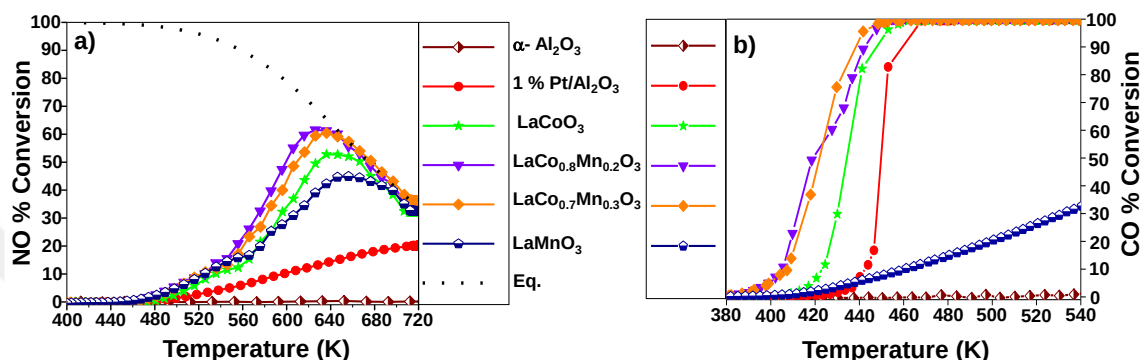


**Figure 4-24.** Catalytic (a) NO oxidation (700 ppm NO(g) and 8 % O<sub>2</sub>(g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 6 K.min<sup>-1</sup>, GHSV = 50,000 h<sup>-1</sup>), (b) CO oxidation (1.6% CO(g) and 20% O<sub>2</sub>(g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 4 K.min<sup>-1</sup>, GHSV = 100,000 h<sup>-1</sup>) test results for selected perovskites and 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark PGM catalyst.

Noticeably, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> appears to be the most promising catalytic architecture due to its intrinsic catalytic properties providing the highest NO oxidation activity (62 % NO conv. at 626 K) and the lowest T<sub>50</sub> of 420 K for CO oxidation. Considering the corresponding reaction temperature intervals of these two different oxidation reactions, it can be argued that the results given in **Figure 4-24a** and **Figure 4-24b** are very good illustrations of suprafacial and intrafacial processes, where 100 % CO conversion in CO oxidation reaction was completed at a lower temperature of ca. 440-460 K and the highest NO oxidation rate was achieved at 626 K.

In order for an accurate comparison of the catalytic activity of the investigated catalytic materials, comparing the number of converted molecules per time and per mass of the catalyst (*i.e.*, specific reaction rate, SRR, see **Sections 3.18.1** and **3.18.2**) can be exploited. Associated experimental parameters such as the reaction temperature, percent conversion and VHSV (Volume Hour Space Velocity)/GHSV (Gas Hour Space Velocity) values for the former studies in the literature are also listed in **Table 4-7** (for the CO oxidation reaction) and **Table 4-8** (for the NO oxidation reaction). Note that, SRR values with  $\mu\text{mol (CO/NO).gcat}^{-1}.\text{s}^{-1}$  units was chosen in this work to compare the ultimate catalytic

activities of the currently investigated perovskite catalysts and the former perovskite catalysts reported in the literature.

Analysis of the results given in **Figure 4-24** indicates that while the maximum conversion in NO oxidation reaction (**Figure 4-24a**) on the investigated perovskites is observed at a relatively high temperature of 626 K, CO oxidation reaction can reach 100 % conversion at much lower temperatures such as 440 K. This can be considered as an indication of the significant differences in the reaction mechanisms and activation routes of these two distinct oxidation processes on perovskite surfaces. Relatively lower temperatures required for CO oxidation on the investigated samples and characteristically linear Arrhenius plots (**Figure 4-25**) obtained from the CO conversion data given in **Figure 4-24b** indicate that LH-type mechanisms [49], [52], [84], [86], [87] may be dominant for the CO oxidation on the perovskite catalysts as well as on the PGM benchmark catalyst. However, as will be shown later in the current text via in-situ spectroscopic measurements, in the case of CO oxidation on perovskites within 380-470 K, formation of surface oxygen vacancies triggering MvK [230] type mechanisms cannot be ruled out as a minor route.

CO conversion vs. temperature profiles of all investigated perovskite samples (except  $\text{LaMnO}_3$ ) and the PGM benchmark catalyst show resemblances in terms of their general line shapes (**Figure 4-24b**). On the other hand, this is not the case for NO oxidation (**Figure 4-24a**), where PGM catalyst reveals a dissimilar NO conversion vs. temperature profile as compared to that of perovskites. This is due to the fact that 1 wt. %  $\text{Pt/Al}_2\text{O}_3$  PGM benchmark catalyst does not possess reducible sites and is incapable of surface/bulk oxygen vacancy generation which is required for the operation of MvK-type mechanisms. Thus, both CO and NO oxidation reactions are likely to proceed exclusively via LH type mechanisms on PGM based  $\text{Pt/Al}_2\text{O}_3$  [231], [232].

**Figure 4-24a** also suggests that at  $T < 550$  K, PGM and perovskite catalysts have similar NO conversion line shapes. However, an abrupt change in NO conversion line shapes is clearly visible for perovskites at  $T > 550$  K, possibly suggesting the dominance of the MvK mechanism. This is due to a drastic change in the electronic structure of the perovskite systems and facilitation of bulk oxygen vacancy formation at these temperatures, which

ultimately alter the surface chemistry of the catalysts to modify the rate determining step, reaction rate orders, and overall kinetics. This argument was already further elaborated in the previous sections via a multitude of in-situ spectroscopic experiments indicating the activation of lattice oxygen species and bulk oxygen vacancy formation on the investigated perovskites that are initiated at 500-600 K. Also, it should be noted that as expected, control experiments performed with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> which is used as a catalyst diluent in the flow reactor yielded practically no activity in CO and NO oxidation reactions (**Figures 4-24a** and **4-24b**). Arrhenius plots for the CO/NO oxidation catalytic tests presented in **Figure 4-24a** are also given in **Figure 4-25** and **Figure 4-26**. Apparent activation energy ( $E_{app}$ ) values obtained from these plots do not simply correlate with the activity trends observed in **Figure 4-24a**, as the mathematically complex nature of the  $E_{app}$  values do not presumably reflect the activation energy value(s) associated with the critical step(s) of the reaction mechanism.

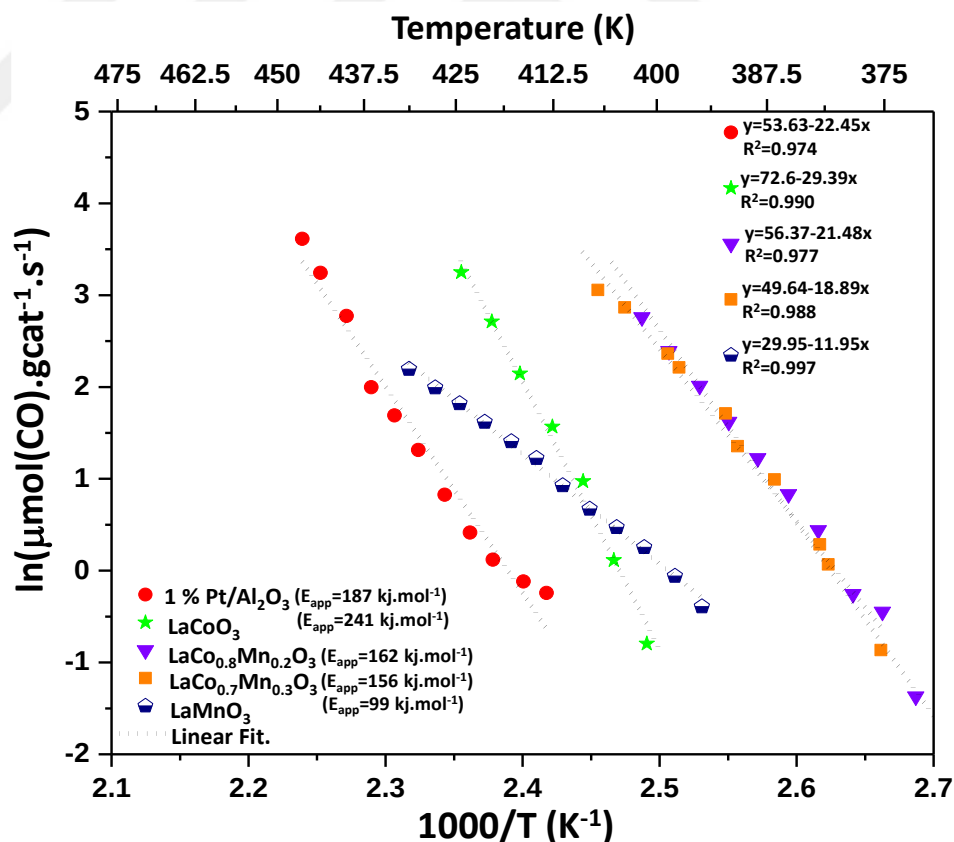


**Figure 4-25.** Arrhenius plots corresponding to the current catalytic CO oxidation performance tests for 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>, LaCoO<sub>3</sub>, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub>, LaCo<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>3</sub>, and LaMnO<sub>3</sub>.

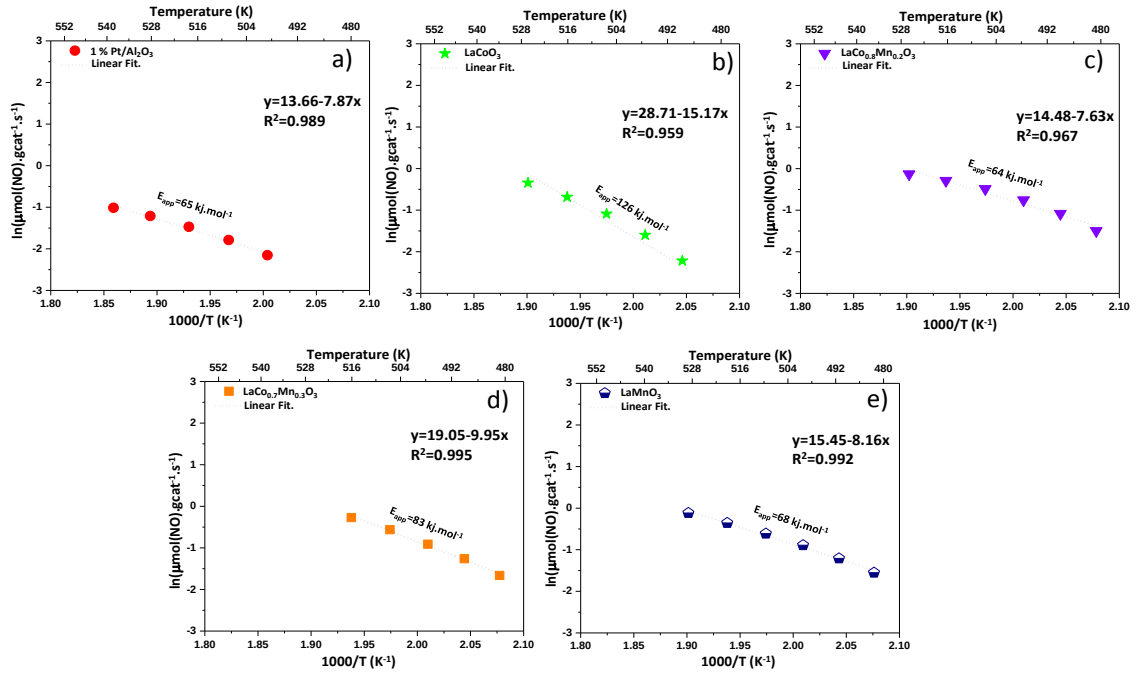


**Figure 4-26.** Arrhenius plots corresponding to the current catalytic NO oxidation performance tests for a) 1 wt. % Pt/ $\text{Al}_2\text{O}_3$ , b)  $\text{LaCoO}_3$ , c)  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ , d)  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ , and e)  $\text{LaMnO}_3$ .

**Table 4-7.** Catalytic CO oxidation comparison for perovskite and PGM based materials.

| Catalyst Number | Catalyst Name                                | $\mu\text{mol}$<br>CO.gcat <sup>-1</sup> .s <sup>-1</sup><br>CO<br>conv. | Temperature<br>(K) | % CO<br>Conversion | GHSV<br>(h <sup>-1</sup> )/<br>VHSV(cm <sup>3</sup><br>STP.g <sup>-1</sup> .h <sup>-1</sup> /N<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> )               | CO<br>Conc. | O <sub>2</sub><br>Conc. | Ref<br>No. |
|-----------------|----------------------------------------------|--------------------------------------------------------------------------|--------------------|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------------------|------------|
| 1               | 1 wt. Pt/ $\text{Al}_2\text{O}_3$            | 148.80                                                                   | 470                | 100%               | 100,000<br>h <sup>-1</sup> /750,000<br>cm <sup>3</sup><br>STP.<br>g <sup>-1</sup> .h <sup>-1</sup><br>1/805,000 N cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 1.6%        | 20%                     | This Work  |
| 2               | 1% wt. Pd/ $\text{Al}_2\text{O}_3$           | 83.18                                                                    | 391                | 100%               | 240,000<br>h <sup>-1</sup> /480,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                            | 1.5%        | 17.6%                   | [95]       |
| 3               | Pt/1% $\text{Al}_2\text{O}_3$                | 24.80                                                                    | 505                | 100%               | 17,000 h <sup>-1</sup> /80,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                 | 1.0%        | 10%                     | [233]      |
| 4               | 1.5% wt. Pt/ $\text{Al}_2\text{O}_3$         | 14.88                                                                    | 573                | 100%               | 120,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup><br>1                                                                                                      | 1.0%        | 1.0%                    | [234]      |
| 5               | 1.5% wt. Pt/ $\text{Al}_2\text{O}_3$         | 1.86                                                                     | 550                | 100%               | 30,000 h <sup>-1</sup> /150,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 0.1%        | 6.0%                    | [235]      |
| 6               | $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ | 148.80                                                                   | 452                | 100%               | 100,000 h <sup>-1</sup> /750,000<br>cm <sup>3</sup><br>STP.<br>g <sup>-1</sup> .h <sup>-1</sup><br>1/805,000 N cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>    | 1.6%        | 20%                     | This Work  |

|    |                                                                                                  |                    |     |      |                                                                                        |   |      |       |       |
|----|--------------------------------------------------------------------------------------------------|--------------------|-----|------|----------------------------------------------------------------------------------------|---|------|-------|-------|
| 7  | LaMnO <sub>3</sub>                                                                               | 83.18              | 716 | 100% | 240,000 h <sup>-1</sup> /<br>480,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | N | 1.5% | 17.6% | [95]  |
| 8  | LaCoO <sub>3</sub>                                                                               | 83.18              | 588 | 100% | 240,000 h <sup>-1</sup> /<br>480,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | N | 1.5% | 17.6% | [95]  |
| 9  | LaCoO <sub>3</sub> (F500)                                                                        | 74.40              | 573 | 100% | 600,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                              |   | 1.0% | 1.0%  | [234] |
| 10 | VO-OM<br>La <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>0.85</sub> O <sub>3</sub>                   | 53.14              | 473 | 100% | 400,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                              |   | 1.0% | 5.0%  | [86]  |
| 11 | 6H-BaFeO <sub>2.78</sub><br>(O <sub>2</sub> (5%)523 K)                                           | 29.76              | 720 | 100% | 240,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                              |   | 1.0% | 0.6%  | [90]  |
| 12 | LaFe <sub>0.8</sub> Cu <sub>0.2</sub> O <sub>3-L</sub>                                           | 29.76              | 546 | 100% | 22,500 h <sup>-1</sup> /<br>48,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>   |   | 5.0% | 20%   | [230] |
| 13 | La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub>                                             | 22.78 <sup>a</sup> | 573 | 98%  | 6,000 h <sup>-1</sup> /12,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>     |   | 16%  | 32%   | [236] |
| 14 | La <sub>0.8</sub> Ag <sub>0.2</sub> MnO <sub>3</sub>                                             | 12.26              | 553 | 99%  | 10,000 h <sup>-1</sup> /99,860<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>    |   | 1.0% | Air   | [237] |
| 15 | LaFe <sub>0.1</sub> Ni <sub>0.9</sub> O <sub>3</sub>                                             | 11.68              | 600 | 100% | 94,200 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 2.0%  | [238] |
| 16 | LaCoO <sub>3</sub>                                                                               | 11.16              | 502 | 100% | 22,500 h <sup>-1</sup> /18,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>    |   | 5.0% | 20%   | [239] |
| 17 | La <sub>0.91</sub> Ce <sub>0.10</sub> Co <sub>0.99</sub> O <sub>3</sub>                          | 11.16              | 377 | 100% | 22,500 h <sup>-1</sup> /18,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>    |   | 5.0% | 20%   | [239] |
| 18 | LaCo <sub>0.95</sub> Pd <sub>0.05</sub> O <sub>3</sub><br>(Stage3)                               | 8.93               | 453 | 100% | 12,000 cm <sup>3</sup> STP.<br>g <sup>-1</sup> .h <sup>-1</sup>                        |   | 6.0% | 4.4%  | [240] |
| 19 | La <sub>0.8</sub> Ce <sub>0.2</sub> MnO <sub>3</sub>                                             | 8.93               | 485 | 100% | 72,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 1.0%  | [241] |
| 20 | La <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>0.8</sub> Cu <sub>0.2</sub> O <sub>3</sub><br>(Cit3) | 7.44               | 628 | 100% | 30,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 2.0% | 1.0%  | [242] |
| 21 | La <sub>0.5</sub> Sr <sub>0.5</sub> CoO <sub>3-d</sub>                                           | 7.44               | 748 | 100% | 60,000 cm <sup>3</sup> STP.<br>g <sup>-1</sup> .h <sup>-1</sup>                        |   | 1.0% | 6.0%  | [243] |
| 22 | LaCo <sub>0.9</sub> Mg <sub>0.1</sub> O <sub>3</sub><br>(LCM3)                                   | 7.44               | 464 | 100% | 96,000 h <sup>-1</sup> /<br>120,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>  |   | 0.5% | 10%   | [88]  |
| 23 | La <sub>0.4</sub> Sr <sub>0.6</sub> CoO <sub>3</sub> -Sr-H <sup>+</sup>                          | 7.44               | 373 | 100% | 60,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 20%   | [244] |
| 24 | La <sub>0.3</sub> Sr <sub>0.7</sub> CoO <sub>3</sub>                                             | 7.44               | 492 | 100% | 60,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 20%   | [45]  |
| 25 | LaCoO <sub>3</sub>                                                                               | 5.03               | 600 | 98%  | 11,600 h <sup>-1</sup> /20,700<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>    |   | 2.0% | 1.0%  | [245] |
| 26 | La <sub>0.1</sub> Sr <sub>0.9</sub> CrO <sub>3</sub>                                             | 4.96               | 623 | 100% | 40,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 2.0%  | [246] |
| 27 | (3DOM) LaCoO <sub>3</sub>                                                                        | 4.95 <sup>b</sup>  | 460 | 100% | 40,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 20%   | [89]  |
| 28 | LaCoO <sub>3</sub>                                                                               | 3.72               | 443 | 100% | 30,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 4.0%  | [247] |
| 29 | La <sub>0.3</sub> Sr <sub>0.7</sub> Ti <sub>0.5</sub> Fe <sub>0.5</sub> O <sub>3+δ</sub>         | 3.53               | 576 | 95%  | 30,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                               |   | 1.0% | 4.0%  | [248] |
| 30 | NiMnO <sub>3</sub>                                                                               | 3.10               | 578 | 100% | 5,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                |   | 5.0% | 5.0%  | [249] |

|    |                                                         |        |     |      |                                                                                                                                                                  |      |      |           |
|----|---------------------------------------------------------|--------|-----|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|-----------|
| 31 | $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (60 min)   | 2.98   | 723 | 100% | $120,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                   | 0.2% | 10%  | [250]     |
| 32 | $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (CC5)      | 2.27   | 573 | 100% | $10,000 \text{ h}^{-1}/12,200 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                              | 1.5% | 21%  | [251]     |
| 33 | $i\text{-YMnO}_3$                                       | 1.86   | 623 | 100% | $30,000 \text{ h}^{-1}/150,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                             | 0.1% | 6.0% | [235]     |
| 34 | $\text{LaFeO}_3$ (Porous)                               | 1.82   | 673 | 98%  | $30,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                    | 0.5% | 7.5% | [252]     |
| 35 | $\text{LaCoO}_3$                                        | 1.49   | 500 | 100% | $12,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                        | 1.0% | 20%  | [253]     |
| 36 | $\text{LaCrO}_3$                                        | 1.49   | 600 | 100% | $12,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                        | 1.0% | 20%  | [254]     |
| 37 | ZLaFe-12 ( $\text{LaFeO}_3/\text{ZrO}_2$ )              | 1.5    | 663 | 100% | $12,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                        | 1.0% | 20%  | [255]     |
| 38 | $\text{LaAl}_{0.7}\text{Fe}_{0.3}\text{O}_3$            | 1.5    | 658 | 100% | $12,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                        | 1.0% | 20%  | [256]     |
| 39 | $\text{LaMnO}_3$                                        | 1.39   | 577 | 100% | $12,000 \text{ N cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                  | 1.0% | 20%  | [257]     |
| 40 | $\text{LaSrCoO}_4$                                      | 1.30   | 493 | 100% | $3,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                     | 3.5% | 7.0% | [258]     |
| 41 | $\text{LaCoO}_{3-8}$                                    | 0.37   | 463 | 100% | $3,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                     | 1.0% | 21%  | [69]      |
| 42 | $\text{BaCe}_{0.90}\text{Pd}_{0.10}\text{O}_{3-\delta}$ | 0.37   | 573 | 93%  | $30,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$                                                                                                    | 0.1% | 10%  | [259]     |
| 43 | $\text{LaCoO}_3$                                        | 148.80 | 460 | 100% | $100,000 \text{ h}^{-1}/750,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}/805,000 \text{ N cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ | 1.6% | 20%  | This Work |
| 44 | $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$            | 148.80 | 452 | 100% | $100,000 \text{ h}^{-1}/750,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}/805,000 \text{ N cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ | 1.6% | 20%  | This Work |
| 43 | $\text{LaMnO}_3$                                        | 145.80 | 773 | 98%  | $100,000 \text{ h}^{-1}/750,000 \text{ cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}/805,000 \text{ N cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ | 1.6% | 20%  | This Work |

<sup>a</sup>In this study, the amount of catalyst for CO ox. reactions was reported as 250 mg however, 400 mg is also reported in the main text and figure captions hence, 250 mg was used for our calculations [236].

<sup>b</sup>The VHSV stated was  $10,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  but from given data calculated space velocity is around  $40,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  by using catalyst mass and flow rate of 0.05 g and 33.3 mL/min respectively.

**Table 4-8.** Catalytic NO oxidation comparison for perovskite and PGM based materials.

| Catalyst Number | Catalyst | $\mu\text{mol NO} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ NO Conv. | Temperature K | NO % Conversion | GHSV ( $\text{h}^{-1}$ )/VHSV ( $\text{cm}^3 \text{ STP} \cdot \text{g}^{-1} \cdot \text{h}^{-1}/\text{N cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ ) | NO Conc. (PPM) | O <sub>2</sub> Conc. | Ref No. |
|-----------------|----------|---------------------------------------------------------------------|---------------|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|----------------------|---------|
|-----------------|----------|---------------------------------------------------------------------|---------------|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|----------------------|---------|

|    |                                                                                                  |                   |     |       |                                                                                                                                                                     |                  |     |              |
|----|--------------------------------------------------------------------------------------------------|-------------------|-----|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-----|--------------|
| 1  | 1% wt. Pt/Al <sub>2</sub> O <sub>3</sub>                                                         | 1.76              | 723 | 20%   | 50,000 h <sup>-1</sup><br>1/1,000,000 cm <sup>3</sup><br>STP.g <sup>-1</sup> .h <sup>-1</sup><br>1/1,073,000 N<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 700              | 8%  | This<br>Work |
| 2  | 1% wt. Pt/Al <sub>2</sub> O <sub>3</sub>                                                         | 1.60              | 603 | 68%   | 375,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 500              | 5%  | [260]        |
| 3  | Commercial DOC<br>(1.6 Pt/0.2 Pt g.liter <sup>-1</sup> )                                         | 0.8 <sup>a</sup>  | 623 | 61%   | 30,000 h <sup>-1</sup> /<br>263,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                               | 400              | 8%  | [32]         |
| 4  | 1.5% wt. Pt-15%<br>BaO/Al <sub>2</sub> O <sub>3</sub>                                            | 0.55              | 637 | 37%   | 123,500 h <sup>-1</sup><br>1/240,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                              | 500              | 6%  | [261]        |
| 5  | LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub>                                             | 5.46              | 626 | 62%   | 50,000 h <sup>-1</sup><br>1/1,000,000 cm <sup>3</sup><br>STP.g <sup>-1</sup> .h <sup>-1</sup><br>1/1,073,000 N<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 700              | 8%  | This<br>Work |
| 6  | LaMnO <sub>3</sub>                                                                               | 1.34              | 623 | 62%   | 30,000 h <sup>-1</sup> /445,500<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 400              | 8%  | [41]         |
| 7  | La <sub>0.9</sub> Sr <sub>0.1</sub> CoO <sub>3</sub>                                             | 1.12 <sup>a</sup> | 568 | 86%   | 30,000 h <sup>-1</sup> /<br>263,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                               | 400              | 8%  | [32]         |
| 8  | 50 wt. %<br>La <sub>0.7</sub> Sr <sub>0.3</sub> CoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> | 1.08              | 623 | 72.4% | 240,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 500              | 6%  | [262]        |
| 9  | BaMn <sub>0.7</sub> Cu <sub>0.3</sub> O <sub>3</sub><br>(BMC3)                                   | 1.00              | 673 | 43%   | 375,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 500              | 5%  | [260]        |
| 10 | La <sub>0.9</sub> Ba <sub>0.1</sub> CoO <sub>3</sub>                                             | 0.83              | 538 | 93%   | 180,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 400              | 10% | [263]        |
| 11 | LaCo <sub>0.9</sub> Cu <sub>0.1</sub> O <sub>3</sub>                                             | 0.73              | 583 | 82%   | 180,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 400              | 10% | [264]        |
| 12 | La <sub>0.7</sub> Sr <sub>0.3</sub> MnO <sub>3</sub><br>(cat-1, flow rate 600<br>mL/min)         | 0.57              | 473 | 32%   | 180,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 800              | 5%  | [265]        |
| 13 | La <sub>0.7</sub> Sr <sub>0.3</sub> CoO <sub>3</sub>                                             | 0.51              | 573 | 82.5% | 123,500 h <sup>-1</sup> /76,080<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 650              | 6%  | [266]        |
| 14 | LaCoO <sub>3</sub> -8                                                                            | 0.48              | 583 | 64%   | 120,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 500 <sup>b</sup> | 10% | [69]         |
| 15 | La <sub>0.9</sub> Sr <sub>0.1</sub> MnO <sub>3</sub>                                             | 0.40              | 623 | 64.9% | 123,500 h <sup>-1</sup> /76,080<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 650              | 6%  | [266]        |
| 16 | LaNi <sub>0.7</sub> Co <sub>0.3</sub> O <sub>3</sub>                                             | 0.38              | 590 | 76%   | 200,000 h <sup>-1</sup><br>1/102,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                              | 400              | 6%  | [267]        |
| 17 | La <sub>0.7</sub> Sr <sub>0.3</sub> CoO <sub>3</sub>                                             | 0.35              | 573 | 74.1% | 80,000 h <sup>-1</sup> /48,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                 | 800              | 5%  | [268]        |
| 18 | LaMnO <sub>3</sub>                                                                               | 0.32              | 623 | 58%   | 90,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                            | 500              | 5%  | [269]        |
| 19 | La <sub>0.7</sub> Ce <sub>0.3</sub> CoO <sub>3</sub>                                             | 0.29              | 583 | 78%   | 37,500 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                            | 800              | 8%  | [270]        |
| 20 | La <sub>0.9</sub> MnO <sub>3</sub>                                                               | 0.27              | 569 | 85%   | 30,000 h <sup>-1</sup> /255,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 100              | 10% | [91]         |
| 21 | La <sub>0.9</sub> Ca <sub>0.1</sub> MnO <sub>3</sub>                                             | 0.26              | 567 | 82%   | 30,000 h <sup>-1</sup> /255,000<br>cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                | 100              | 10% | [271]        |
| 22 | LaMn <sub>0.9</sub> Co <sub>0.1</sub> O <sub>3</sub>                                             | 0.24              | 553 | 76.5% | 255,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                                                           | 100              | 10% | [272]        |

|    |                                                                 |      |     |       |                                                                                                                                                           |     |    |           |
|----|-----------------------------------------------------------------|------|-----|-------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----|-----------|
| 23 | Cr-doped Ce <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub> -EG | 0.06 | 623 | 66.3% | 35,400 h <sup>-1</sup> /255,000 cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup>                                                                         | 390 | 8% | [273]     |
| 24 | LaCoO <sub>3</sub>                                              | 4.66 | 636 | 53%   | 50,000 h <sup>-1</sup> /1,000,000 cm <sup>3</sup> STP.g <sup>-1</sup> .h <sup>-1</sup><br>1/1,073,000 N cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 700 | 8% | This Work |
| 25 | LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub>            | 5.28 | 636 | 60%   | 50,000 h <sup>-1</sup> /1,000,000 cm <sup>3</sup> STP.g <sup>-1</sup> .h <sup>-1</sup><br>1/1,073,000 N cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 700 | 8% | This Work |
| 26 | LaMnO <sub>3</sub>                                              | 3.96 | 656 | 45%   | 50,000 h <sup>-1</sup> /1,000,000 cm <sup>3</sup> STP.g <sup>-1</sup> .h <sup>-1</sup><br>1/1,073,000 N cm <sup>3</sup> .g <sup>-1</sup> .h <sup>-1</sup> | 700 | 8% | This Work |

<sup>a</sup>Instead of washcoat loading of DOC catalyst, density of slurry for wash coating (0.114 g/ml) was reported, and the loaded active catalyst amount was found by using washcoat slurry density for 3.2 ml monolith volume (calculated by using monolith size and space velocity) [32]

<sup>b</sup>The NO conc. was found from the NO conv. graph.

In **Table 4-7** and **Table 4-8**, three different Space Velocity (SV) units are shown I) GHSV (h<sup>-1</sup>), II) VHSV (cm<sup>3</sup> STP.g<sup>-1</sup>.h<sup>-1</sup>), and III) VHSV (N cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup>). The first SV unit GHSV (h<sup>-1</sup>) is found by calculating the ratio of the total flow volume in 1 h over catalyst bed volume. The remaining space velocity definitions have exactly the same units (STP and N are used to specify identical environmental conditions). To accurately calculate space velocities, flow rates need to be reported with their environmental conditions such as Standard Temperature and Pressure (STP) and Normal Temperature and Pressure (N), where STP and N stand for 760 Torr, 273 K and 760 Torr, 293 K, respectively. However, in **Table 4-7** and **Table 4-8**, SV values in some of the literature work is given with cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup> units. This means that environmental conditions were not specified in these reports. Hence,  $\mu\text{mol (CO/NO).gcat}^{-1}.\text{s}^{-1}$  values were calculated from the presented data in these studies assuming STP conditions. Additionally, to prepare an easy-to-compare list, the highest CO % conversion values at the lowest temperatures were chosen from the previous and current studies to emphasize not only the highest oxidation rate but also the minimal thermal activation capability.

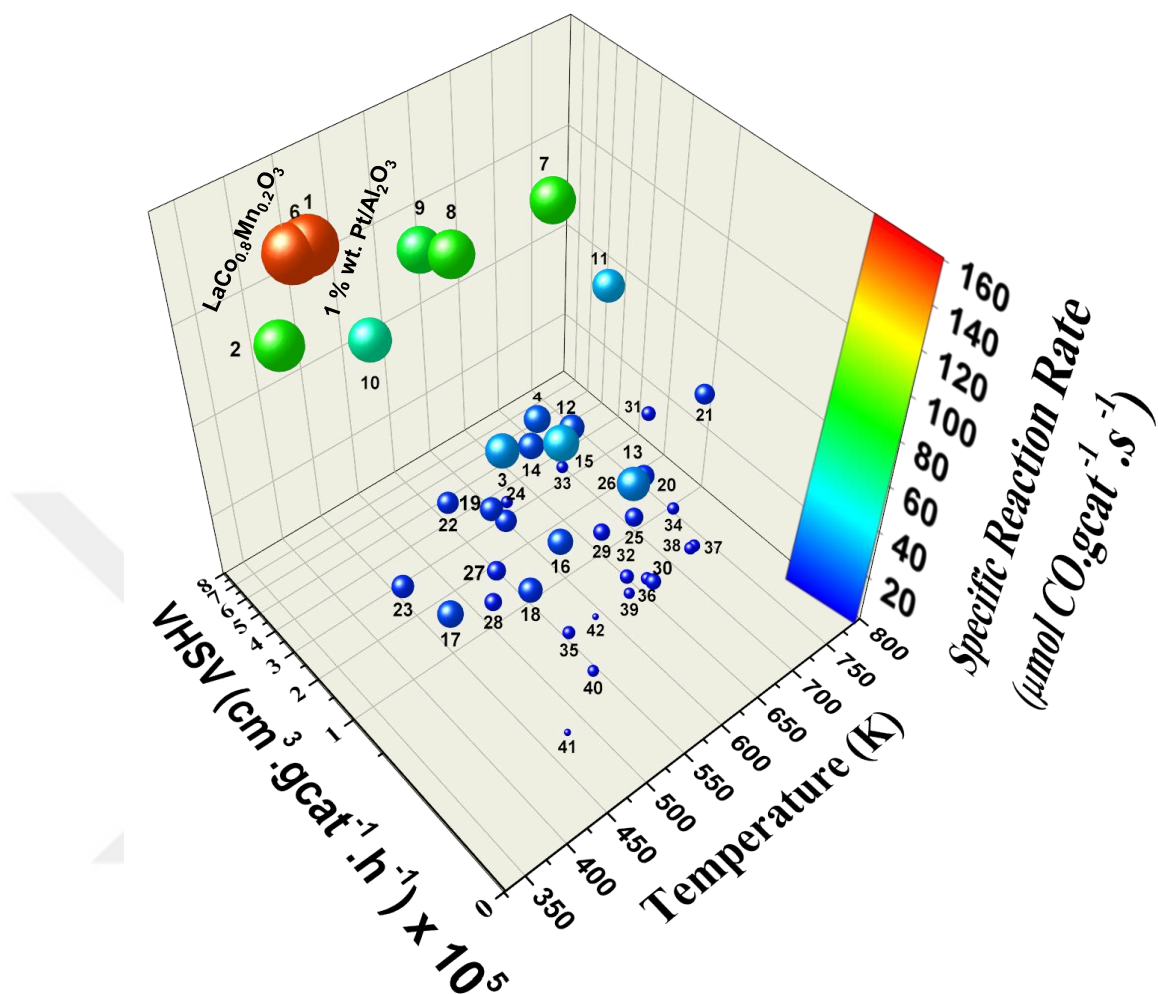


**Figure 4-27.** Multi-variable (SRR, VHSV, and Temperature) CO oxidation performance comparison of Catalyst (1) (i.e., 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub>, this work) and Catalyst (6) (i.e., LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub>, this work) with former studies. For detailed information, see **Table 4-7**. Identification of the catalysts 1-42 are also given in **Table 4-7**.

In **Figure 4-27** and **Figure 4-28** graphically illustrates the catalytic CO oxidation and NO oxidation performances the existing perovskite catalysts in the literature with that of the currently investigated catalysts by considering more than one performance parameters. The catalytic oxidation results point out that LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> does not only exhibit the highest SRR for NO oxidation (**Figure 4-27**), but also shows the highest SRR for CO oxidation (**Figure 4-28**) along with the lowest light-off temperature. Note that LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> has the lowest T<sub>50</sub> temperature among other catalysts studied in this study including 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> (**Figure 4-24b**).

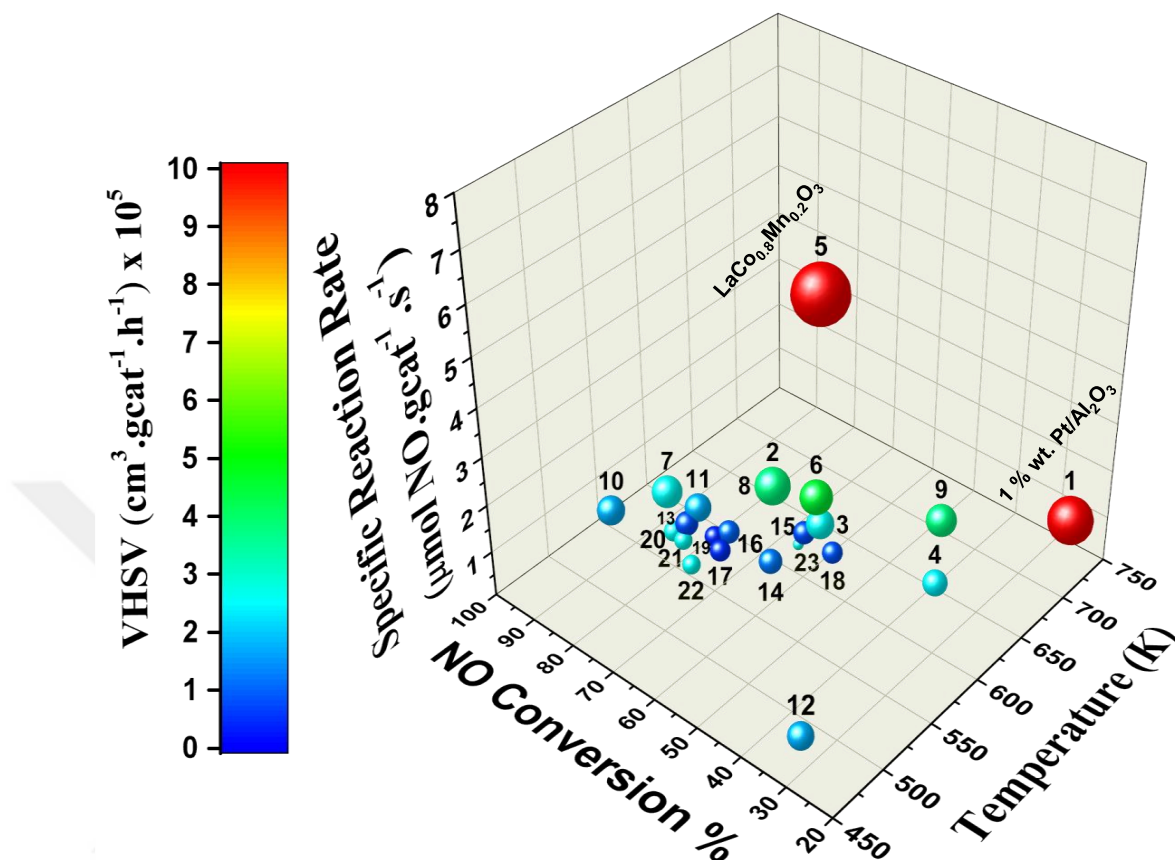


**Figure 4-28.** Multi-variable (SRR, VHSV, NO % conversion and, Temperature) NO oxidation performance demonstration of Catalyst (1) (i.e., 1wt.% Pt/Al<sub>2</sub>O<sub>3</sub>, this work), and Catalyst (5) (i.e., LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub>, this work) with former studies. For detailed information, see **Table 4-8**. Identification of the catalysts 1-23 are also given in **Table 4-8**).

The CO oxidation rate of LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> was found to be **148.8 μmol CO.gcat<sup>-1</sup>.s<sup>-1</sup>** at 100 % conversion and this value is almost two times greater than the closest PGM based conventional catalysts demonstrated in previous studies (see **Table 4-8**). Moreover, as indicated in **Table 4-8**, NO oxidation rate of LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> (**5.46 μmol NO.gcat<sup>-1</sup>.s<sup>-1</sup>**) is 1.7 times higher than the most active PGM based catalyst and more than four times higher as compared to most active NO oxidation perovskite catalyst reported in literature [41]. To the best of our knowledge, LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> demonstrates the highest catalytic NO and CO oxidation activity based on SRR (**μmol CO/NO.gcat<sup>-1</sup>.s<sup>-1</sup>**) as compared to PGM based conventional and PGM-free perovskite catalysts (see **Table 4-7** and **Table 4-8**).

Long-term isothermal catalytic durability results given in **Figure 4-29a** indicate that the initial % NO conversion attained by the LaCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> B-site mixed perovskite catalyst

is suppressed only to a limited extent after 28 h of catalyst operation. These results demonstrate that the  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  B-site mixed perovskite possesses long term NO oxidation capability and does not undergo a drastic catalytic aging within 28 h of the catalytic reaction. Similar isothermal longevity tests for CO oxidation at 410 K (**Figure 4-29b**) suggest that B-site mixed perovskite can retain CO conversion during the first 28 h of the catalytic reaction without a major decrease in catalytic activity.

$\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  can be considered as the optimized catalyst for CO oxidation and NO oxidation reactions when compared to its PGM-based and PGM-free counterparts. On the other hand, by considering the inlet NO and CO concentrations of the conventional diesel engine exhaust systems, it can be realized that the SRR values reported in this study are much more higher than these former studies in terms of  $\mu\text{mol CO/NO.gcat}^{-1}.\text{s}^{-1}$  (**Figure 4-27** and **Figure 4-28**). On the other hand, as it was mentioned in **Section 1.3.1.2.3**, the maximum SCR performance is obtained when the  $\text{NO}_2$  comprises 60 % of the total  $\text{NO}_x$  species for the fast SCR processes [30].  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  catalyst reported in the current work yields 62 % NO conversion at 626 K. Thus, the  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  can be considered as a promising PGM-free alternative DOC not only because of its high oxidation capability but also its optimized  $\text{NO}_2/\text{NO}_x$  ratio to produce maximum  $\text{N}_2$  via fast SCR. Additionally, high oxidation capability of the perovskites under currently chosen harsh catalytic conditions implies that perovskite based oxidation catalysts are promising potential candidates not only in mobile applications (*e.g.*, transportation) but also in stationary sources such as power plants working with fossil fuels.

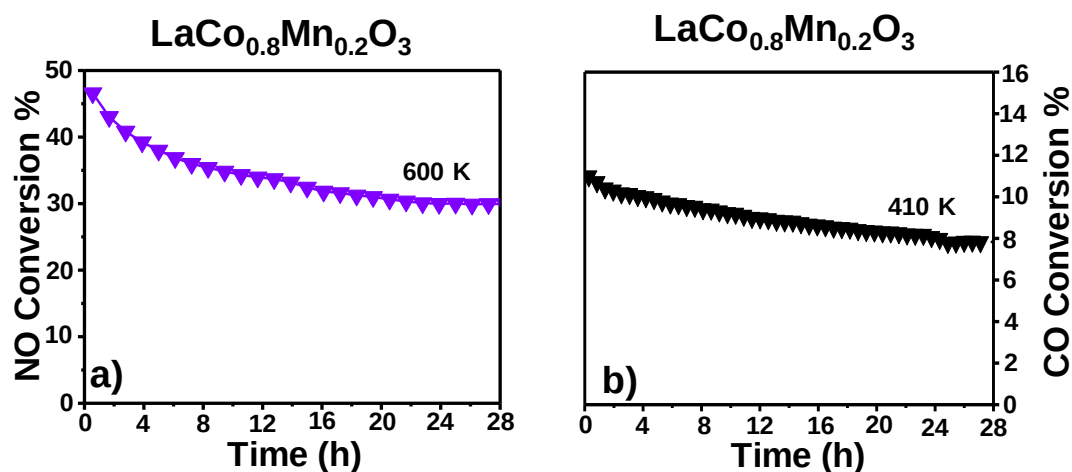


**Figure 4-29.** Long term NO and CO oxidation catalytic performance tests on  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ .

The only difference in the catalytic stability experiments given in **Figure 4-29** was the reaction temperatures, which was chosen to be 600 K for NO and 563 K for CO oxidation. These reaction temperatures represent the lowest temperatures for the highest catalytic NO or CO conversions obtained on the  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  catalyst. The results given in **Figure 4-29** indicate that  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  can sustain its oxidation capability for extended durations of time. On the other hand, there is a significant decrease in NO oxidation activity of  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ . After 20 h of operation, NO conversion reaction rate was found to converge to a stable value of ca. 30 %. It is also important to emphasize that although 30 % NO conversion may seem to represent a low catalytic activity, in terms of its corresponding SRR value, it still has the highest NO oxidation activity (**Table 4-7**). Furthermore, during long-term CO oxidation experiment,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  shows high durability by reaching steady state at 8 % CO conversion.

It is apparent that  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$  and  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  show extremely high catalytic oxidation capability. However,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  demonstrates slightly higher oxidation capability than that of  $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ . Previous studies report that  $\text{Co}^{3+}$  cations behave as Lewis acid sites and are extremely crucial for CO adsorption [274]–[276]. Also, the formation of  $\text{Co}^{2+}$  was stated to be important in the generation of superoxo ( $\text{O}_2^-$ ) species as a result of molecular oxygen adsorption on oxygen vacancies. Hence, a high CO oxidation activity may be a consequence of the synergistic operation of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  sites [274]–[276].

## **4.2. Fe/CeO<sub>2</sub>, Co/CeO<sub>2</sub>, and Co-Fe/CeO<sub>2</sub> SCR Catalysts for NO Reduction**

### **4.2.1. Flow Mode Catalytic NO Reduction Tests on Fe/CeO<sub>2</sub>, Co/CeO<sub>2</sub>, and Co-Fe/CeO<sub>2</sub> Catalysts**

The NO(g) reduction experiments were performed for all samples given in **Table 3-2**. In the current study, the loading effect of Fe on CeO<sub>2</sub> was studied. The samples were prepared with Fe loadings of 1, 2, 4, 6, 8, and 20 wt. % supported on CeO<sub>2</sub>-Type A (for more information on CeO<sub>2</sub>-Type A, see **Appendix B3**). Unless otherwise stated, all CeO<sub>2</sub> supports in this work can be considered as Type A.

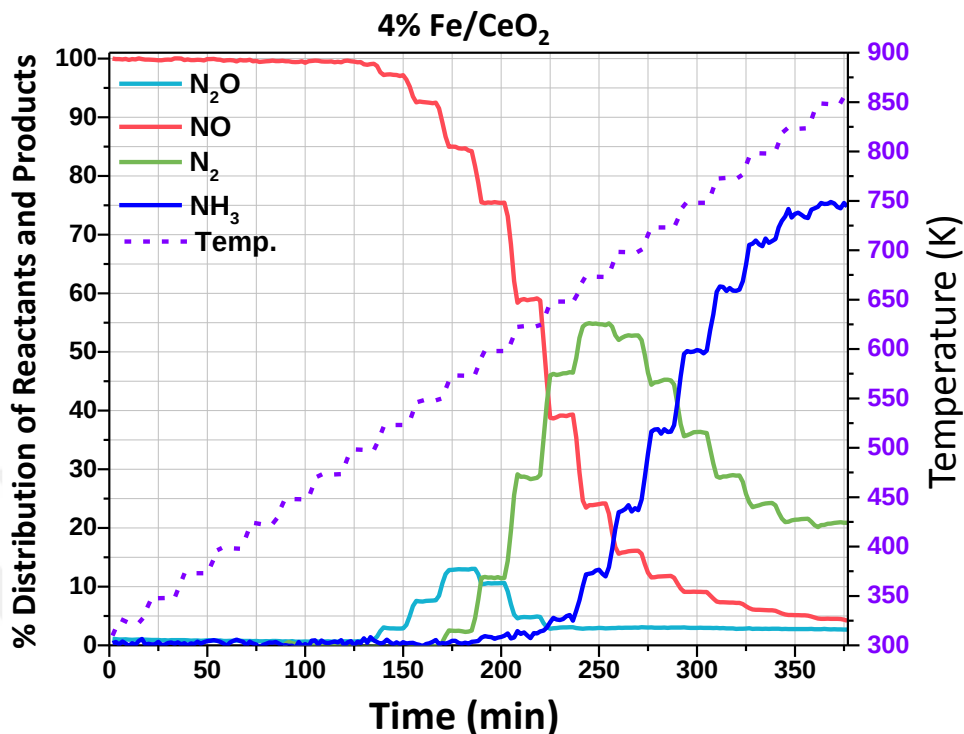


**Figure 4-30.** Flow-mode catalytic NO(g) reduction tests with H<sub>2</sub>(g) for 4% Fe/CeO<sub>2</sub> (8000 ppm NO(g) and 24000 ppm H<sub>2</sub>(g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 5 K.min<sup>-1</sup>, VHSV = 600,000 cm<sup>3</sup>g<sup>-1</sup>.h<sup>-1</sup>).

**Figure 4-30** indicates the catalytic NO reduction test results for 4 wt. Fe/CeO<sub>2</sub> within 300-850 K. It is seen that NO activation starts around 500 K and reaches the maximum conversion at around 800 K. At relatively low temperatures such as 500-550 K (*i.e.*, during the initial stages of NO activation) N<sub>2</sub>O dominates the other reduction products. With increasing temperature, first N<sub>2</sub> becomes the primary product and at higher temperatures, NH<sub>3</sub> overwhelms all other reduction products. Since N<sub>2</sub>O is a toxic greenhouse gas with adverse global warming effects [33], elevated working temperatures can be chosen for this SCR catalyst to yield low N<sub>2</sub>O emission.

Investigation of the catalytic NO reduction performance in terms of SRR yields a total NO spill over rate (inlet concentration of total NO) of **59.5  $\mu\text{mol (NO).gcat}^{-1}.\text{s}^{-1}$**  which is higher than most of the previously studied NO reduction catalysts in the literature [118]. Although ammonia formation is important for NSR incorporated SCR systems, N<sub>2</sub> formation is more crucial as the ultimately desired and potentially harmless final reduction product. Therefore, the lowest operational temperature for the highest NO conversion to N<sub>2</sub> can be the most important performance parameter of the NO reduction catalysts. Our studies on

Fe/CeO<sub>2</sub> catalysts with different Fe loadings within 1-20 wt. % Fe showed that 4 wt. % Fe/CeO<sub>2</sub> catalyst revealed the highest activity (see **Appendix B2** and **Appendix B3**) in terms of both light off temperature and the maximum NO percent conversion.

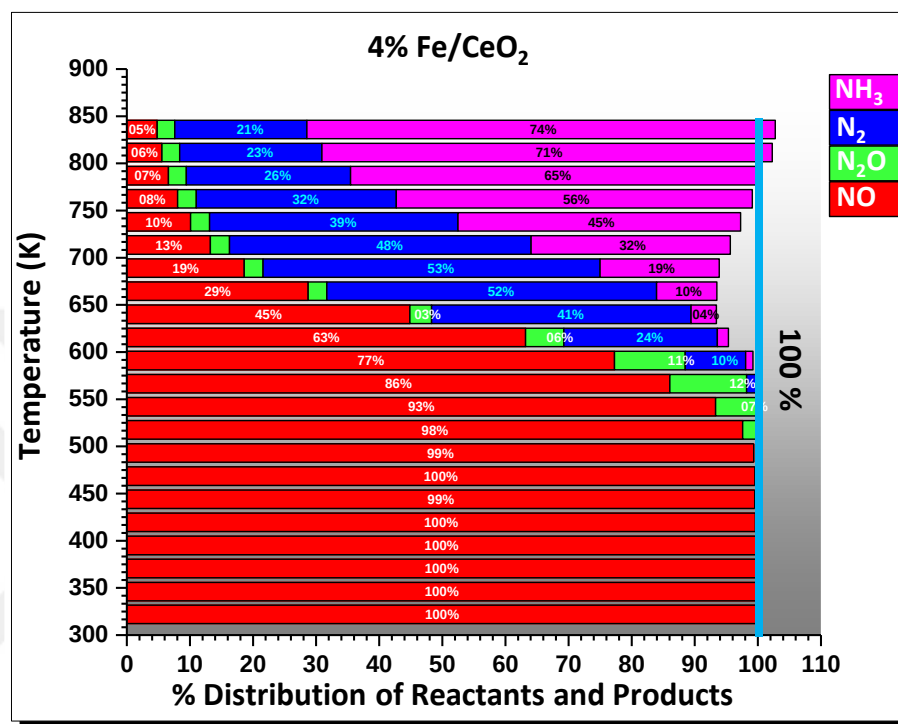


**Figure 4-31.** % NO conversion and distribution of products as a function of temperature in NO reduction with H<sub>2</sub> on the 4 wt. % Fe/CeO<sub>2</sub> catalyst. (8000 ppm NO(g) and 24000 ppm H<sub>2</sub>(g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 5 K.min<sup>-1</sup>, VHSV = 600,000 cm<sup>3</sup>g<sup>-1</sup>.h<sup>-1</sup>).

**Figure 4-31** depicts the product selectivity as a function of NO conversion and reaction temperature in NO reduction with H<sub>2</sub> on 4 wt. % Fe/CeO<sub>2</sub> catalyst. 4 wt. % Fe/CeO<sub>2</sub> catalyst shows the best performance at around 650 K where N<sub>2</sub> production is maximum and the total NO conversion is 71 %. At elevated temperatures, NO conversion continues to increase, but N<sub>2</sub> selectivity is suppressed and NH<sub>3</sub> formation becomes dominant. Formation of N<sub>2</sub>O at low temperatures indicates that N-O bond activation occurs in an incomplete manner at these temperatures, allowing the presence of both NO and atomic N species on the catalyst surface which may get together to form N<sub>2</sub>O, where N has the formal oxidation state of +1. At these low temperatures, H<sub>2</sub> activation is expected to be rather limited preventing the formation of extensively reduced N-containing species such as N<sub>2</sub> (where formal oxidation state of N = 0), or NH<sub>3</sub> (where formal oxidation state of N = -3). On the other hand, with increasing temperatures, with increasing H<sub>2</sub> activation, N-O bond

cleavage starts to occur with a greater extent leading to the complete transformation of adsorbed NO species into atomic N and atomic O species, which lead to the formation of N<sub>2</sub> via recombinative N atom pair desorption. In this reaction regime, H<sub>2</sub> activation is still not high enough to increase the surface coverage of H atoms on the catalyst surface and thus, formation of -NH, -NH<sub>2</sub>, and NH<sub>3</sub> are not favored. On the other hand, atomic O species generated by N-O bond cleavage could interact with chemisorbed H<sub>2</sub> resulting in H<sub>2</sub>O formation. Hence, -NH, -NH<sub>2</sub>, and NH<sub>3</sub> may not be enhanced due to the high selectivity towards water. Finally, at elevated temperatures, both N-O and H-H bond activation events occur with high efficiency on the catalyst surface enabling the formation of -NH, -NH<sub>2</sub>, and NH<sub>3</sub> species, rendering ammonia as the dominant reduction product.

An interesting aspect of **Figure 4-31** is the N-atom mass balance. As a result of N-atom mass balance, the total percent contribution of all N-containing species may be expected to add up to 100 % at any given time (or temperature) during the catalytic NO reduction test. However, it is seen in **Figure 4-31** that the total percent contribution of all N-containing species deviates from 100 % (**Figure 4-31**). In the low NO % conversion regime (*i.e.*,  $T < 600$  K), mass balance seems to be conserved. However, with increasing NO % conversion and formation of NH<sub>3</sub> species within 600-750 K, it is seen that not all of the N-atoms entering the reactor leave the reactor as N-containing products. This observation suggests the storage/adsorption of N-containing species in the form of -NH, -NH<sub>2</sub>, and NH<sub>3</sub> species on the catalyst surface at these moderate temperatures. In contrast, at  $T > 750$  K, this time it is observed that N-atoms leaving the reactor is more than that of the N-atoms entering the reactor. This observation indicates that at these high temperatures, N-atoms which are stored on the catalyst surface in the form of -NH, -NH<sub>2</sub>, and NH<sub>3</sub> species start to desorb.

**Table 4-9.** The comparison of  $N_2$  selectivity % for different Fe/CeO<sub>2</sub> catalysts and 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark.

| Sample Name                               | Highest % N <sub>2</sub> Selectivity | Temperature (K) for Highest N <sub>2</sub> Selectivity (T <sub>N2</sub> )* | NO % Conversion at T <sub>N2</sub> |
|-------------------------------------------|--------------------------------------|----------------------------------------------------------------------------|------------------------------------|
| Bare CeO <sub>2</sub>                     | 20                                   | 850                                                                        | 53                                 |
| 1 wt. % Fe/CeO <sub>2</sub>               | 29                                   | 737                                                                        | 51                                 |
| 2 wt.% Fe/CeO <sub>2</sub>                | 29                                   | 687                                                                        | 47                                 |
| 4 wt. % Fe/CeO <sub>2</sub>               | 52                                   | 662                                                                        | 71                                 |
| 6 wt. % Fe/CeO <sub>2</sub>               | 36                                   | 687                                                                        | 62                                 |
| 8 wt. % Fe/CeO <sub>2</sub>               | 38                                   | 712                                                                        | 59                                 |
| 20 wt. % Fe/CeO <sub>2</sub>              | 30                                   | 662                                                                        | 56                                 |
| 1 wt. % Pt/Al <sub>2</sub> O <sub>3</sub> | 20                                   | 525                                                                        | 93                                 |

\*T<sub>N2</sub> is the temperature at which N<sub>2</sub> selectivity is the highest.

**Table 4-9** lists the highest N<sub>2</sub> selectivity, temperature for the highest N<sub>2</sub> selectivity, and the NO conversion % at T<sub>N2</sub> for Fe/CeO<sub>2</sub> catalysts with varying Fe loadings. These results indicate that 4 wt. % Fe/CeO<sub>2</sub> catalyst is a promising catalyst that can convert NO selectively into N<sub>2</sub>, which is the primarily desired reduction product [277]–[279]. Although Fe based catalysts have promising catalytic activity for NO to N<sub>2</sub> conversion, the Pt based benchmark catalyst still shows superior catalytic activity especially in terms of lower NO activation temperature and higher NO conversion % at T<sub>N2</sub> (**Table 4-9**).

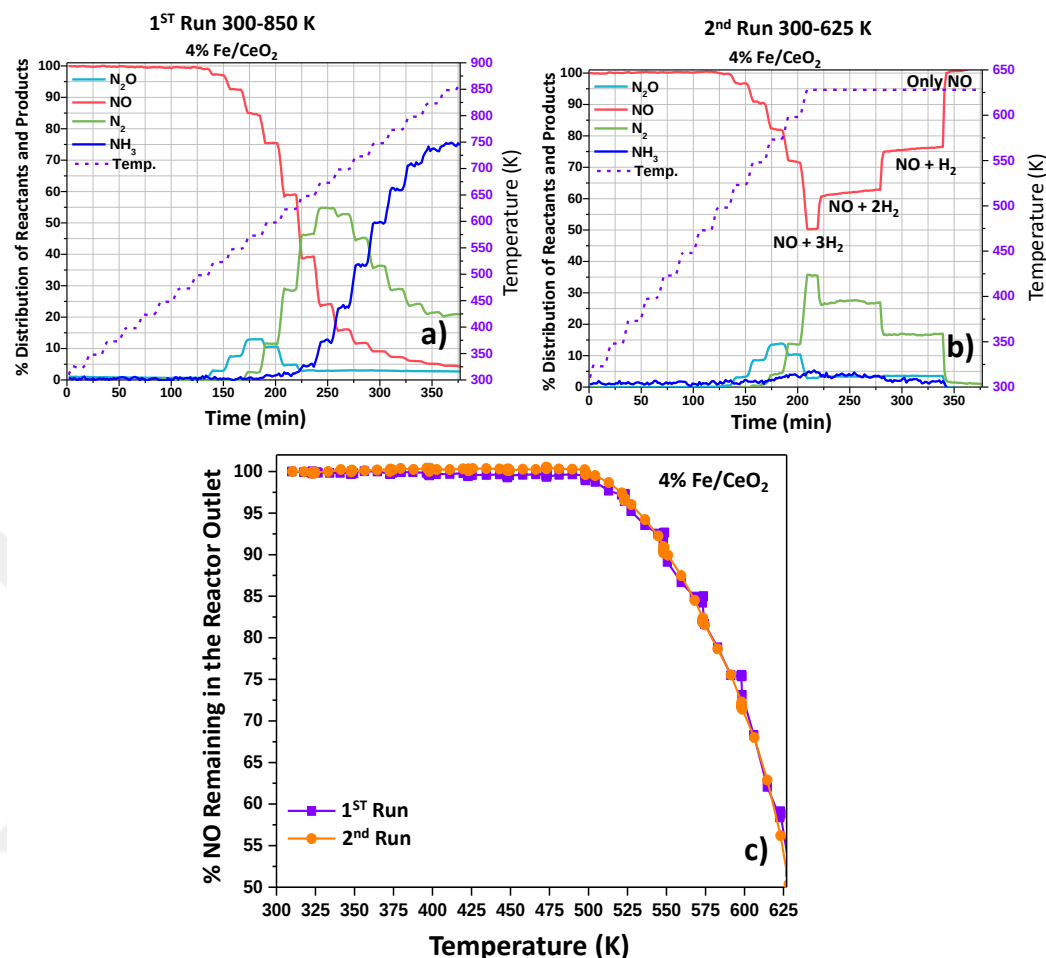


**Figure 4-32.** NO reduction with H<sub>2</sub> on 4% Fe/CeO<sub>2</sub> catalyst. a) Constant reactant feed composition of NO(g)/H<sub>2</sub>(g) = 1/3 within 300-850 K, b) Repetition of the 1<sup>st</sup> run with a reactant feed composition of NO(g)/H<sub>2</sub>(g) = 1/3 within 300-625 K, followed by reaction under NO(g)/H<sub>2</sub>(g) = 1/2, and NO(g)/H<sub>2</sub>(g) = 1/1 feed compositions at 625 K. c) Demonstration of the catalytic reproducibility in the 1<sup>st</sup> and 2<sup>nd</sup> runs with a reactant feed composition of NO(g)/H<sub>2</sub>(g) = 1/3 within 300-625 K.

NO reduction with H<sub>2</sub> on Pt-based catalysts has been extensively studied [277]–[280]. In these former experimental and kinetic studies, it was reported that N<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub>O are the main products and product selectivity can be altered by modifying NO/H<sub>2</sub> ratio and reaction temperature. The previous studies on Pt/Rh-based catalysts showed that N<sub>2</sub>O is a low-temperature product and its production decreases as a function of increasing temperature where N<sub>2</sub> and NH<sub>3</sub> become dominant products. N<sub>2</sub> selectivity is the highest at moderate temperatures and NH<sub>3</sub> becomes the overwhelming product at relatively high temperatures [277]–[279]. A similar behavior can be observed for currently investigated metal oxide-based catalysts given in **Figure 4-30** and **Figure 4-31**. In the experiments given in **Figure 4-30** and **Figure 4-31**, NO/H<sub>2</sub> ratio was set to 1/3. Therefore, to observe

the  $\text{H}_2(\text{g})$  concentration effect on selectivity,  $\text{NO}/\text{H}_2$  ratio was varied from 1/3 to 1/2, and eventually to 1/1 (see **Section 3.18.4.3** for more details) in additional experiments given in **Figure 4-32**. As expected, decreasing the amount of  $\text{H}_2$  in the reactant feed decreases the  $\text{NH}_3$  formation and increases the selectivity toward  $\text{N}_2$ .

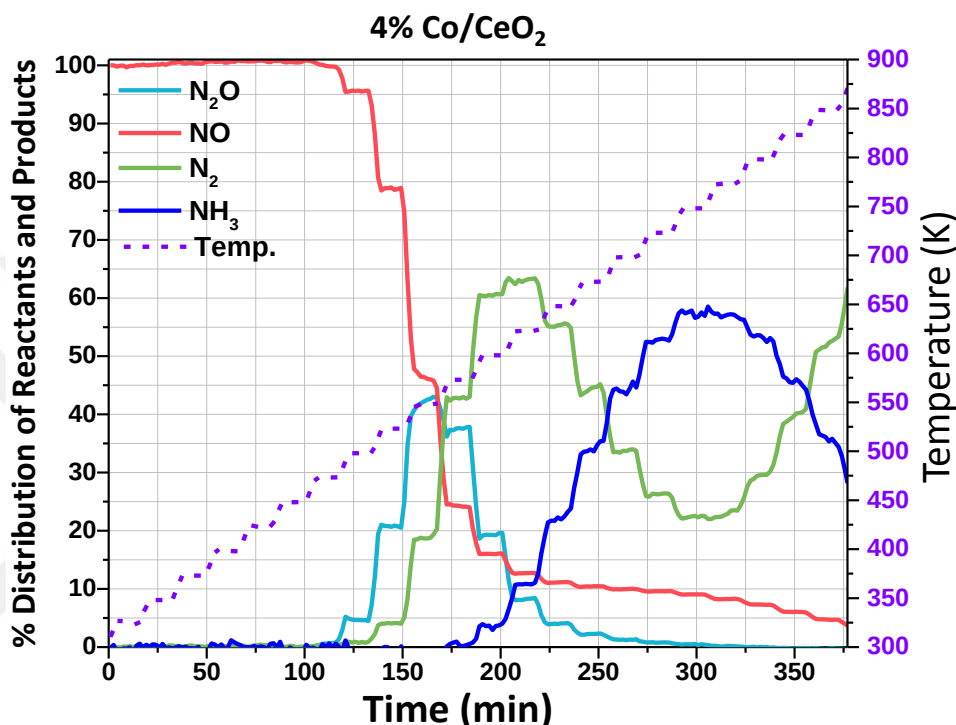


**Figure 4-33.** Flow-mode  $\text{NO}(\text{g})$  reduction with  $\text{H}_2(\text{g})$  results for 4 wt.%  $\text{Co}/\text{CeO}_2$  (8000 ppm  $\text{NO}(\text{g})$  and 24000 ppm  $\text{H}_2(\text{g})$  in  $\text{Ar}(\text{g})$ , total flow rate =  $500 \text{ ml STP} \cdot \text{min}^{-1}$ , heating rate  $5 \text{ K} \cdot \text{min}^{-1}$ , VHSV =  $600,000 \text{ cm}^3 \text{g}^{-1} \cdot \text{h}^{-1}$ )

**Figure 4-33** reveals the results of temperature dependent NO reduction with  $\text{H}_2$  for 4 wt. %  $\text{Co}/\text{CeO}_2$  catalyst. The 4 wt. % Co metal loading was intentionally chosen based on the NO conversion performance of 4 wt. % Fe loaded  $\text{CeO}_2$ . However, to ensure that the 4 wt. % Co loaded samples has the highest performance as compared to other Co loadings, 2, 6, and 8 wt. % Co loaded  $\text{Co}/\text{CeO}_2$  catalysts were also studied in temperature dependent NO reduction tests (see **Appendix B4**).

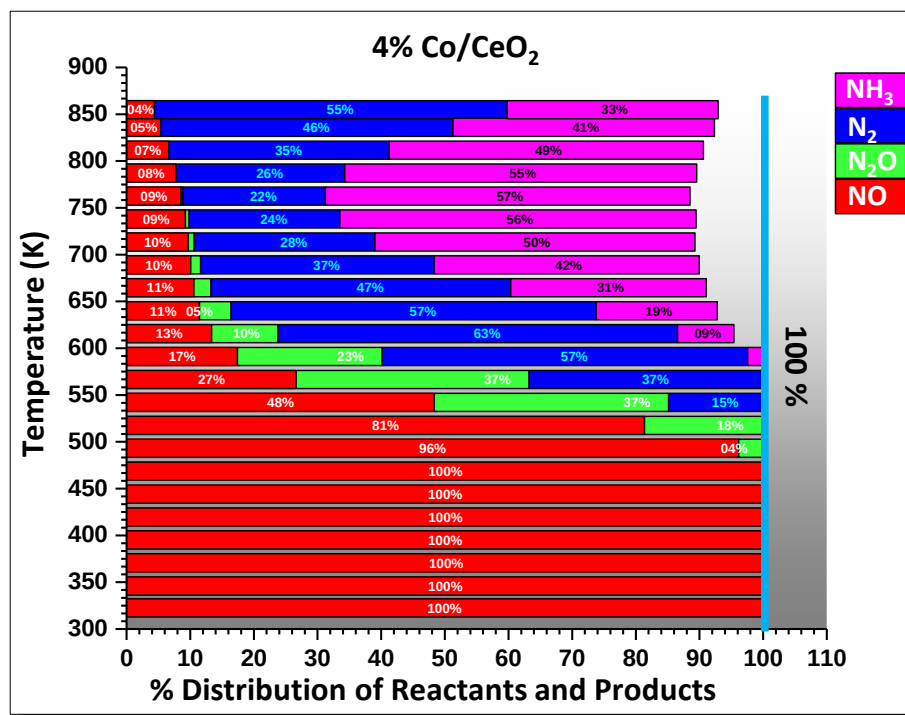


**Figure 4-34.** % NO conversion and distribution of products as a function of temperature in NO reduction with H<sub>2</sub> on the 4 wt. % Co/CeO<sub>2</sub> catalyst. (8000 ppm NO(g) and 24000 ppm H<sub>2</sub>(g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 5 K.min<sup>-1</sup>, VHSV = 600,000 cm<sup>3</sup>g<sup>-1</sup>.h<sup>-1</sup>).

As seen in **Figure 4-34**, NO conversion starts around 475 K on the 4 wt. % Co/CeO<sub>2</sub> catalyst suggesting a lower temperature for the beginning of N-O bond activation as compared to that of 4 wt. % Fe/CeO<sub>2</sub> catalyst (525 K). **Figure 4-34** shows that N<sub>2</sub>O has the highest selectivity at low temperatures, while N<sub>2</sub> becomes the predominant reduction product at moderate temperatures and high temperatures favor NH<sub>3</sub>. However, unlike 4 wt. % Fe/CeO<sub>2</sub> catalyst, in the case of 4 wt. % Co/CeO<sub>2</sub>, extremely high temperatures result in the suppression of the NH<sub>3</sub> selectivity at the expense of increasing N<sub>2</sub> selectivity. While the selectivity trends at low, moderate and high temperatures can be explained in an analogous manner to the 4 wt. % Fe/CeO<sub>2</sub> case, the different selectivity pattern for 4 wt. % Co/CeO<sub>2</sub> at extremely high temperatures can be explained by the consumption of hydrogen on the 4 wt. % Co/CeO<sub>2</sub> catalyst surface, where CoO<sub>x</sub> and/or CeO<sub>2</sub> domains are reduced by H<sub>2</sub> leaving limited concentration of available H atoms for further reduction of adsorbed N species to -NH, -NH<sub>2</sub>, and NH<sub>3</sub>.

Some of the possible mechanistic in the NO reduction with H<sub>2</sub> on Fe/CeO<sub>2</sub> and Fe/CeO<sub>2</sub> catalysts are listed below (\*adsorption/active site on catalyst):

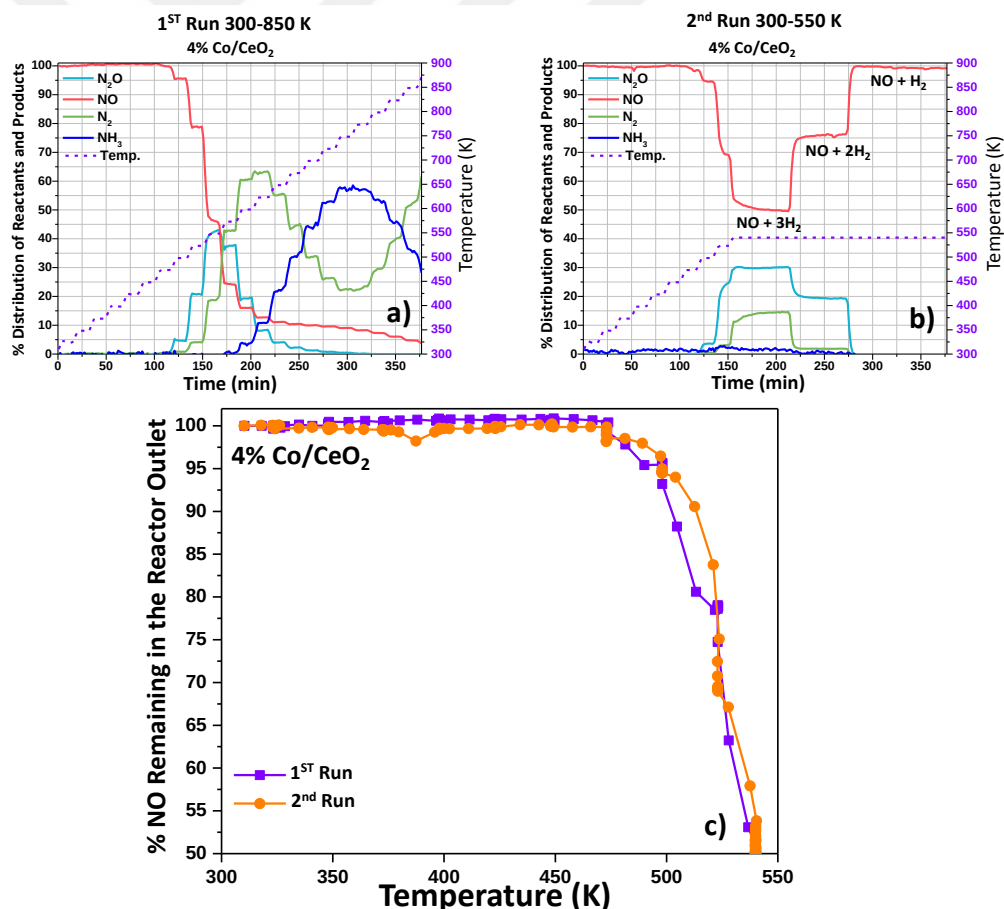


**Figure 4-35.** NO reduction with H<sub>2</sub> on 4 wt. % Co/CeO<sub>2</sub> catalyst. a) Constant reactant feed composition of NO(g)/H<sub>2</sub> (g) = 1/3 within 300-850 K, b) Repetition of the 1<sup>st</sup> run with a reactant feed composition of NO(g)/H<sub>2</sub> (g) = 1/3 within 300-635 K, followed by reaction under NO(g)/H<sub>2</sub> (g) = 1/2, and NO(g)/H<sub>2</sub> (g) = 1/1 feed compositions at 535 K. c) Demonstration of the catalytic reproducibility in the 1<sup>st</sup> and 2<sup>nd</sup> runs with a reactant feed composition of NO(g)/H<sub>2</sub> (g) = 1/3 within 300-535 K.

The **Figure 4-32b** and **Figure 4-35b** indicate that the direct NO decomposition in the absence (**Figure 4-32**) of H<sub>2</sub> is not possible due to 100 % non-converted NO signal. Furthermore, in **Figure 4-35b**, 4% Co/CeO<sub>2</sub> is not able to convert NO where NO:H<sub>2</sub> stoichiometry is equal to 1:1 thus, the possible N<sub>2</sub>O formation based on the direct NO decomposition indicated in reaction (4-22) cannot be achieved by either Fe or Co based catalysts. Additionally, the reaction kinetics could be significantly different for Co and Fe based catalysts. While Co is not active at low concentrations of H<sub>2</sub>(g), Fe based ceria (see **Figure 4-32b**) still shows some activity even at low H<sub>2</sub>(g) concentrations.

**Table 4-10.** The comparison of Percent N<sub>2</sub> selectivity for different Co loaded CeO<sub>2</sub> catalysts and 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark.

| Sample Name                               | Highest % N <sub>2</sub> Selectivity | Temperature (K) for Highest N <sub>2</sub> Selectivity (T <sub>N2</sub> )* | NO % Conversion at T <sub>N2</sub> |
|-------------------------------------------|--------------------------------------|----------------------------------------------------------------------------|------------------------------------|
| 4 wt. % Fe/CeO <sub>2</sub>               | 52                                   | 662                                                                        | 71                                 |
| 2 wt. % Co/CeO <sub>2</sub>               | 46                                   | 612                                                                        | 82                                 |
| 4 wt. % Co/CeO <sub>2</sub>               | 63                                   | 612                                                                        | 87                                 |
| 6 wt. % Co/CeO <sub>2</sub>               | 35                                   | 612                                                                        | 64                                 |
| 8 wt. % Co/CeO <sub>2</sub>               | 41                                   | 612                                                                        | 71                                 |
| 1 wt. % Pt/Al <sub>2</sub> O <sub>3</sub> | 20                                   | 525                                                                        | 93                                 |

\*T<sub>N2</sub> is the temperature where N<sub>2</sub> selectivity is the highest.

In **Table 4-10**, the catalytic activity comparison between 4 wt. % Fe/CeO<sub>2</sub> and 4 wt. % Co/CeO<sub>2</sub> is demonstrated with their highest N<sub>2</sub> selectivity and the temperature at highest N<sub>2</sub> formation. The 4 wt. % Co/CeO<sub>2</sub> seems much more efficient than 4 wt. % Fe/CeO<sub>2</sub> due to low temperature NO conversion and high selectivity for N<sub>2</sub> (see **Figure 4-33**). Another crucial point is that 4 wt. % Co/CeO<sub>2</sub> catalyst is also highly selective for N<sub>2</sub>O, which eventually decreases at relatively high temperatures. To explain this, one can consider the relatively higher basicity of CoO<sub>x</sub> [281] as compared to that of FeO<sub>x</sub>. Thus, enhanced NO adsorption on CoO<sub>x</sub> at low temperatures may ultimately produce more N<sub>2</sub>O based on the proposed (4-23), (4-24), and (4-25) reactions.

Addition of Fe and Co onto the different supports was considered due to their NO reduction performance as a single metal-loaded catalyst. On the other hand, the support effect is also studied as a secondary parameter, which can be used to enhance catalytic performance of NO reduction. Therefore, 50 wt. % CeO<sub>2</sub>-ZrO<sub>2</sub>, 9 wt. % La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, 10 wt. % WO<sub>3</sub>-ZrO<sub>2</sub>,

and  $\text{CeO}_2$  supports were used with 4 wt. % Fe-4 wt. % Co metal loading and NO reduction experiments with those catalysts were performed to screen their catalytic contribution for NO conversion (See **Appendix B5**). These experiments revealed that  $\text{CeO}_2$  support showed the best NO reduction performance as compared to other supports (**Table 4-11**).

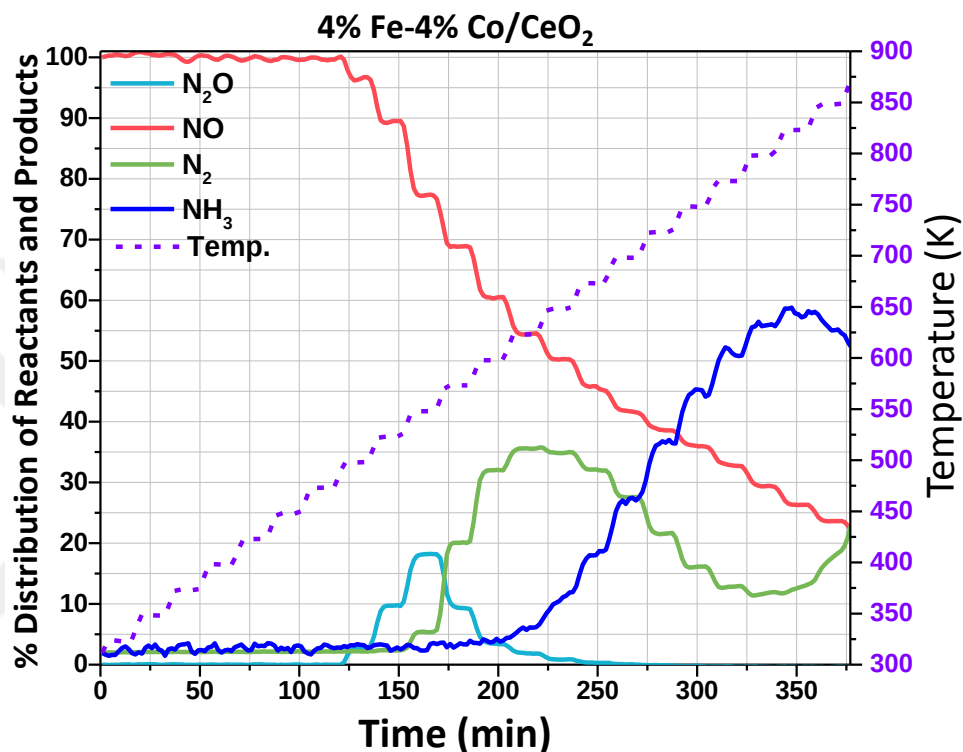


**Figure 4-36.** Flow-mode  $\text{NO(g)}$  reduction with  $\text{H}_2\text{(g)}$  results for 4 wt. % Co - 4 wt. % Fe/ $\text{CeO}_2$  (8000 ppm  $\text{NO(g)}$  and 24000 ppm  $\text{H}_2\text{(g)}$  in  $\text{Ar(g)}$ , total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 5 K.min<sup>-1</sup>, VHSV = 600,000 cm<sup>3</sup>g<sup>-1</sup>.h<sup>-1</sup>).

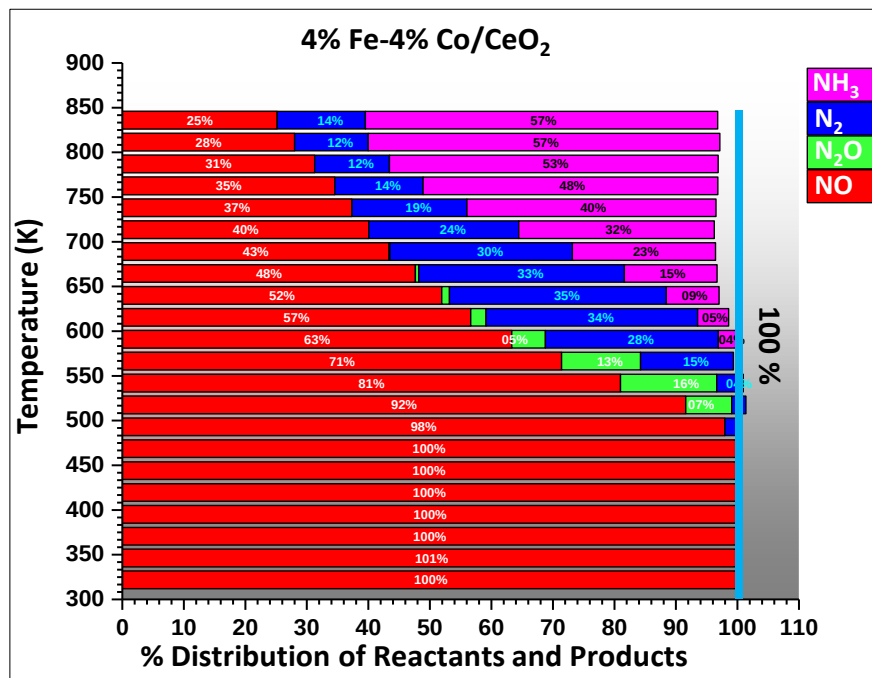


**Figure 4-37.** % NO conversion and distribution of products as a function of temperature in NO reduction with  $H_2$  on the 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub> catalyst. (8000 ppm NO(g) and 24000 ppm  $H_2$ (g) in Ar(g), total flow rate = 500 ml STP.min<sup>-1</sup>, heating rate 5 K.min<sup>-1</sup>, VHSV = 600,000 cm<sup>3</sup>g<sup>-1</sup>.h<sup>-1</sup>).

The **Figure 4-37** exhibits the product and reactant distribution of 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub> catalyst in NO reduction with  $H_2$  as a function of temperature.

**Table 4-11.** The comparison of Percent  $N_2$  selectivity for 4 wt. % Fe-4 wt. % Co loaded on different supports, and 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> benchmark.

| Sample Name                                                            | Highest % $N_2$ Selectivity | Temperature (K) for Highest $N_2$ Selectivity ( $T_{N_2}$ )* | NO % Conversion at $T_{N_2}$ |
|------------------------------------------------------------------------|-----------------------------|--------------------------------------------------------------|------------------------------|
| 4 wt. % Fe/CeO <sub>2</sub>                                            | 52                          | 662                                                          | 71                           |
| 4 wt. % Co/CeO <sub>2</sub>                                            | 63                          | 612                                                          | 87                           |
| 4 wt. % Fe-4 wt. % Co/CeO <sub>2</sub>                                 | 35                          | 637                                                          | 48                           |
| 4 wt. % Fe-4 wt. % Co/WO <sub>3</sub> -ZrO <sub>2</sub>                | 20                          | 762                                                          | 47                           |
| 4 wt. % Fe-4 wt. % Co/La <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> | 25                          | 712                                                          | 48                           |
| 4 wt. % Fe-4 wt. % Co/CeO <sub>2</sub> -ZrO <sub>2</sub>               | 18                          | 662                                                          | 42                           |
| 1 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>                              | 20                          | 525                                                          | 93                           |

\* $T_{N_2}$  is the temperature where  $N_2$  selectivity is the highest.

**Figure 4-38** illustrates the NO reduction behavior of 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub> as a function of  $H_2$ (g) concentration. Based on the results given above, it can be argued that there is no direct NO decomposition (see **Figure 4-38b**). Interestingly, ammonia and

nitrogen levels decrease together, unlike other NO reduction reaction cases where an initial decrease in  $\text{NH}_3$  concentration is observed (see **Appendix B5**).

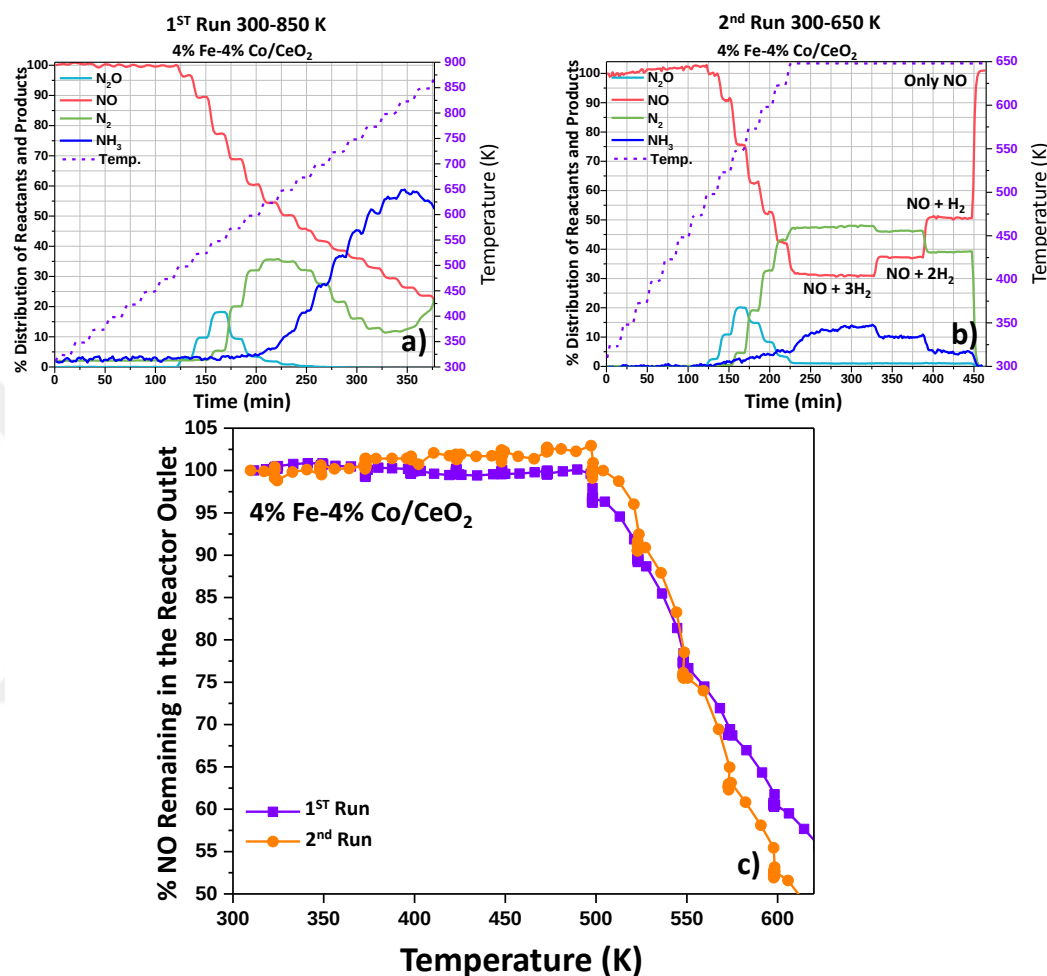


**Figure 4-38.** NO reduction with  $\text{H}_2$  on 4 wt. % Fe-4 wt. % Co/ $\text{CeO}_2$  catalyst. a) Constant reactant feed composition of  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/3$  within 300-850 K, b) Repetition of the 1<sup>st</sup> run with a reactant feed composition of  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/3$  within 300-650 K, followed by reaction under  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/2$ , and  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/1$  feed compositions at 650 K. c) Demonstration of the catalytic reproducibility in the 1<sup>st</sup> and 2<sup>nd</sup> runs with a reactant feed composition of  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/3$  within 300-650 K.

#### 4.2.2. Ex-Situ Characterization of Fe/Co Based $\text{CeO}_2$ Catalysts

The XRD results given in **Figure 4-39** for bare  $\text{CeO}_2$ , 4 wt. % Co/ $\text{CeO}_2$ , 4 wt. % Fe-4 wt. % Co/ $\text{CeO}_2$ , and 4 wt. % Fe/ $\text{CeO}_2$  demonstrate that metallic Fe/Co or  $\text{FeO}_x/\text{CoO}_x$  crystal phases are not detected on the  $\text{CeO}_2$  support. Possible origins of undetectable  $\text{FeO}_x/\text{CoO}_x$  species in XRD can be associated with the small particle/domain size, high surface dispersion, and disorder in these species. Peck et. al. [114] reported that until reaching surface coverages of 9.36 Fe/ $\text{nm}^2$  and 4.84 Co/ $\text{nm}^2$ , no significant change in the XRD

pattern of  $\text{CeO}_2$  support was observed. At higher loadings of Co, a very weak diffraction signal was reported to appear at  $36.8^\circ$ .

The XRD results for other Fe and Co loadings on  $\text{CeO}_2$  as well as on different supports are provided in **Appendix B6** where all these diffraction results are quite similar to the results given in **Figure 4-39**. There is no secondary phase detected other than  $\text{CeO}_2$  or the corresponding support.

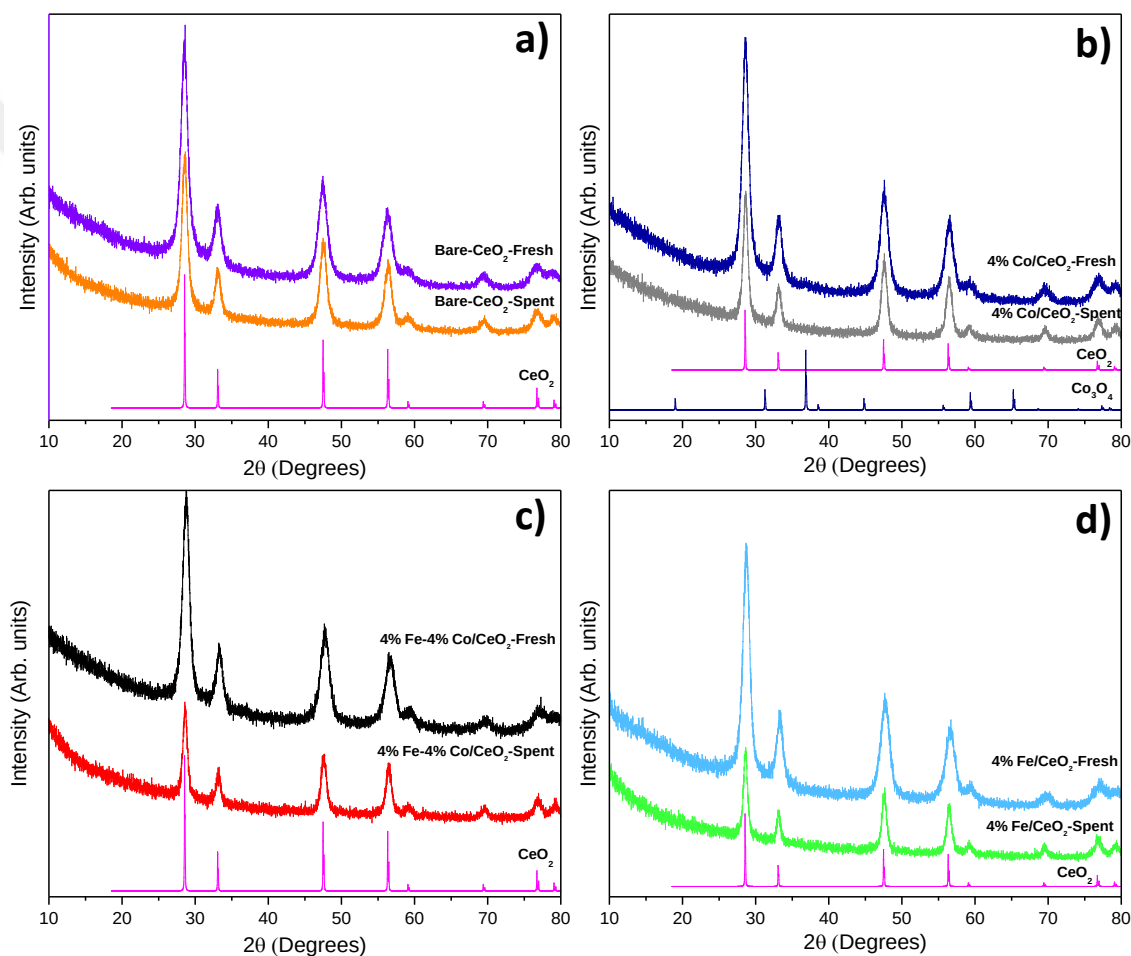


**Figure 4-39.** XRD profiles of a) bare  $\text{CeO}_2$  support, b) 4%  $\text{Co}/\text{CeO}_2$ , c) 4%  $\text{Fe}$ -4%  $\text{Co}/\text{CeO}_2$ , and d) 4%  $\text{Fe}/\text{CeO}_2$  in their fresh and spent (recovered catalyst just after  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/3$  within 300-850 K reaction) forms. The reference  $\text{CeO}_2$  and  $\text{Co}_3\text{O}_4$  have ICDD PDF Card No: 00-004-0593 and 00-0421467, respectively.

ATR-FTIR results for fresh and spent bare  $\text{CeO}_2$ , 4 wt. %  $\text{Fe}/\text{CeO}_2$ , 4 wt. %  $\text{Co}/\text{CeO}_2$ , and 4 wt. %  $\text{Fe}$ -4 wt. %  $\text{Co}/\text{CeO}_2$  catalysts are given in **Figure 4-40**. ATR-FTIR signal at around  $666\text{ cm}^{-1}$ , only visible for Co loaded fresh catalysts, is in line with the presence of  $\text{Co}_3\text{O}_4$  microcrystals on ceria support [114]. Furthermore, the signal around  $666\text{ cm}^{-1}$  is not visible for spent Co loaded catalysts suggesting that during the reduction of  $\text{NO}$ ,  $\text{Co}_3\text{O}_4$

could be reduced. IR signals at 852, 1051 and between 1297-1640  $\text{cm}^{-1}$  can be associated with surface carbonates, and hydrogen carbonates, respectively [282], [283]. Contribution from residual nitrates/nitrites originating from the metal nitrate precursors used in the catalyst synthesis cannot be ruled out either. After the NO reduction experiments, these originally present carbonate/nitrate signals were suppressed and/or shifted for spent catalysts.

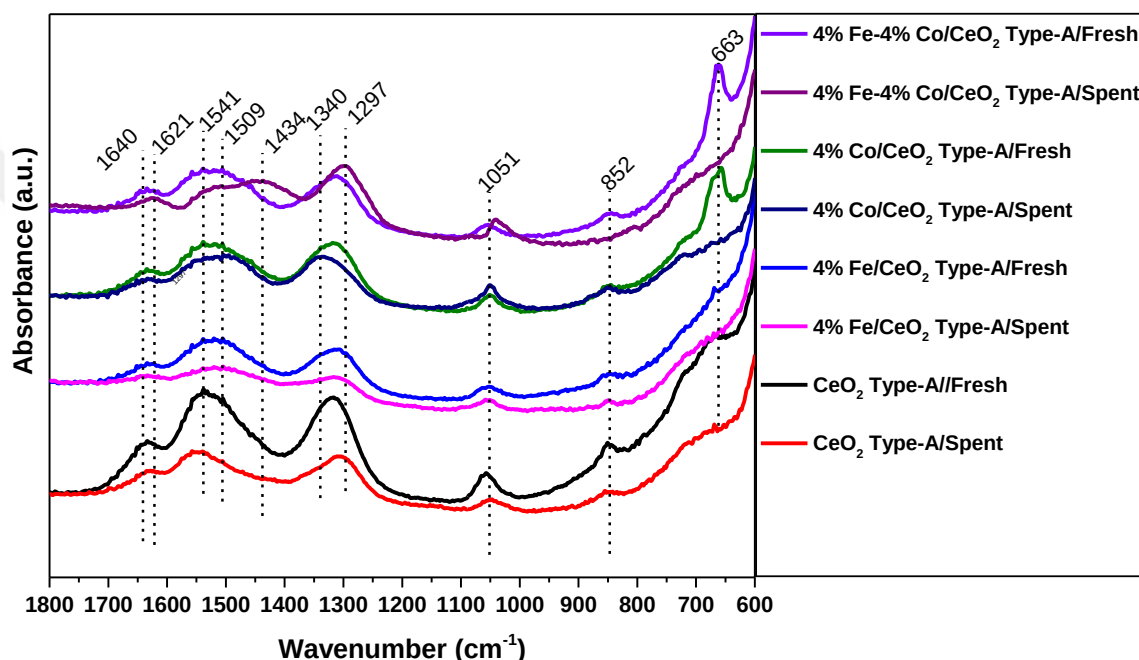


**Figure 4-40.** ATR-FTIR results for bare  $\text{CeO}_2$ , 4% Fe/ $\text{CeO}_2$ , 4% Co/ $\text{CeO}_2$ , and 4% Fe-4% Co/ $\text{CeO}_2$  in their fresh and spent (recovered catalyst just after  $\text{NO(g)}/\text{H}_2(\text{g}) = 1/3$  within 300-850 K reaction) forms.

The SSA results given in **Table 4-12** indicate that Fe and Co loading decreases the surface area of bare ceria. Especially, co-impregnation of Fe/Co on ceria decreases the total surface area more significantly as compared to single metal impregnation. However, based on the catalytic activity results for NO reduction, there is no direct correlation between SSA and the catalytic activity.

**Table 4-12.** Specific surface area (SSA) results for Bare and Fe/Co doped ceria samples in their fresh forms.

| Sample Name                           | SSA $\text{m}^2/\text{g}$ |
|---------------------------------------|---------------------------|
| Bare $\text{CeO}_2$                   | 144                       |
| 4 wt. % Fe/ $\text{CeO}_2$            | 91                        |
| 4 wt. % Co/ $\text{CeO}_2$            | 98                        |
| 4 wt. % Fe-4 wt. % Co/ $\text{CeO}_2$ | 80                        |
| 1 wt. % Pt/ $\text{Al}_2\text{O}_3$   | 165                       |

*Ex-situ* Raman and *in-situ* NO adsorption experiments were also conducted (see **Appendix B7** to **B9**) to find out the correlation in between structure and functionality. However, current findings need to be supported with additional experiments to have a more precise explanation about structural properties of NO reduction catalyst/s.



## CHAPTER 5

### Conclusions

In the current work, a simple and a reproducible synthetic protocol was utilized to synthesize B-site mixed perovskites with a nominal stoichiometry of  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  ( $x = 0.1-0.9$ ), whose bulk B-site stoichiometry, surface/bulk B-site oxidation states, and bulk oxygen vacancy population can be controlled in a gradual manner. Bulk-oxygen vacancies were found to have a strong effect on the redox activity of the B-site mixed perovskites allowing them to efficiently switch between high and low B-site oxidation states in a reversible fashion under relatively moderate redox conditions without requiring elevated temperatures for regeneration, unlike  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  benchmark systems. In these B-site mixed perovskite systems, A-site bulk oxidation state seems to remain intact without presenting a strong influence on reactivity. We also utilized catalytic disproportionation of  $\text{NO}_2(\text{g})$  into surface nitrates/nitrites on the B-site mixed perovskite surfaces as a proof of principle. It is shown that B-site mixed perovskites with a particular bulk-oxygen vacancy population and electronically modified B-site cations with specific oxidation states can yield greater  $\text{NO}_2$  conversion into surface nitrates/nitrites, which may beat single B-site benchmark perovskites such as  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$ . Presumably, this is realized by the diffusion of bulk oxygen vacancies to the surface, which dictate the surface redox reactivity.

It is worth mentioning that these observations cannot be explained simply using geometric parameters such as relative specific surface areas (SSA) of the investigated materials. Obtained B-site mixed perovskites have complex electronic structures and unique surface chemistries. An efficient methodology was presented to estimate entire bulk stoichiometry and the bulk oxygen deficiency of the B-site mixed perovskites by combining average bulk-oxidation state information provided by XANES and bulk A-site and B-site atomic ratios measured in ICP-MS. B-site mixed perovskites possess predominantly  $\text{Co}^{3+}$  and  $\text{Mn}^{4+}$  surface sites with smaller contributions from  $\text{Co}^{2+}$  and  $\text{Mn}^{3+}$  states. These surface oxidation states are also fairly consistent with the average bulk oxidation states (*i.e.*,  $\text{Co}^{2.71+}/\text{Mn}^{3.65+}$  and  $\text{Co}^{2.59+}/\text{Mn}^{3.63+}$  for  $\text{La}_{1.01}\text{Co}_{0.75}\text{Mn}_{0.24}\text{O}_{2.97}$  and  $\text{La}_{1.04}\text{Co}_{0.65}\text{Mn}_{0.31}\text{O}_{2.97}$ , respectively).

Bulk and surface oxidation states of A-sites (*i.e.*,  $\text{La}^{3+}$ ) were found to be identical and also were insensitive to the perovskite composition. Although bulk compositions were compatible with the nominal compositions foreseen from the quantities of precursors used in the synthesis, surfaces of these B-site mixed perovskites were found to be significantly enriched with La and O. Thus, it is likely that on the surface of the investigated materials, in addition to the B-site mixed perovskite phases exhibiting oxygen vacancies, there exists other metal-oxide, metal-hydroxide, metal carbonate phases, which were elusive to identify in a conclusive manner, using the multitude of characterization techniques exploited in the current work (*i.e.*, XRD,  $\text{N}_2$  adsorption-desorption isotherm, ICP-MS, TEM, XPS, *ex-situ* and *in-situ* XANES, EXAFS, *in-situ* FTIR,  $\text{H}_2$ -TPR, and TPD).

On the other hand, flow mode catalytic performance tests indicated that  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  is the optimum and the most durable B-site mixed perovskite for NO/CO oxidation due to its defect mobility under different redox conditions, reversible redox capacity, oxidation state specific cation distribution ( $\text{Co}^{3+}/\text{Co}^{2+}$ ), population of  $e_g$  electronic levels (due to adsorption on vertically oriented  $e_g$  orbitals of coordinately unsaturated surface atoms ( $\text{BO}_5$ )), and surface population of B-site cations. Additionally, in the flow mode catalytic performance tests, currently synthesized affordable B-site mixed perovskites exhibited superior oxidation capability at extremely harsh conditions with extraordinarily high SRR values when compared to other perovskite catalysts from previous studies. In addition, PGM-free  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  exhibited better catalytic NO/CO oxidation activity when compared to conventional 1 wt. % Pt/ $\text{Al}_2\text{O}_3$  precious metal benchmark catalyst. Thus,  $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$  reveal a strong potential to be considered for DOC systems.

The Fe and/or Co based ceria supported SCR systems, which can work in tandem with DOC systems, were also studied to design materials for a complete PGM-free aftertreatment system. In these Fe/Co based SCR systems, we aimed to obtain high NO reduction performance with lowers  $\text{NO}_x$  conversion temperatures and enhanced selective toward  $\text{N}_2$  at high NO inlet concentrations.

In the design of SCR catalysts. Fe and/or Co loading and support effects were separately studied. The 4 wt. % Co/ $\text{CeO}_2$  was found to be the most active catalyst with 63 %  $\text{N}_2$

selectivity at 612 K where total NO conversion is 87 % (with a SRR value of **51.8  $\mu\text{mol (NO).gcat}^{-1}$** ). XRD, N<sub>2</sub> adsorption-desorption isotherm, Raman, and *in-situ* FTIR spectroscopic techniques were utilized to correlate structural differences of 4 wt. % Co/CeO<sub>2</sub> sample with others. Additionally, fresh and spent catalysts were investigated to monitor structural changes and to associate those findings with the NO conversion performance. Based on the spectroscopic characterization results it can be argued that formation of new Co-O-Ce interfacial sites may facilitate NO adsorption as well as N-O and H-H bond activation.



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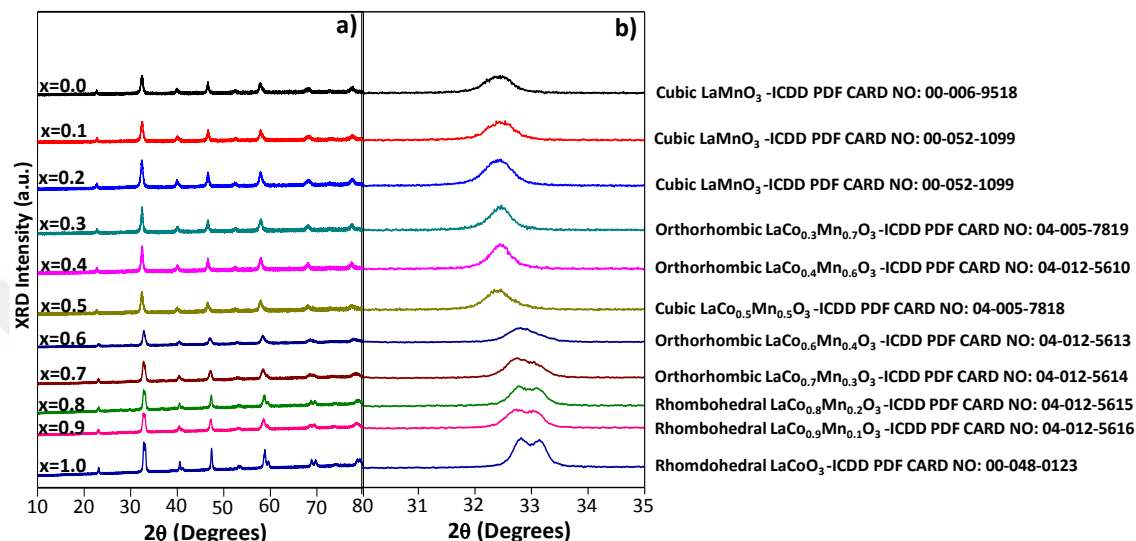
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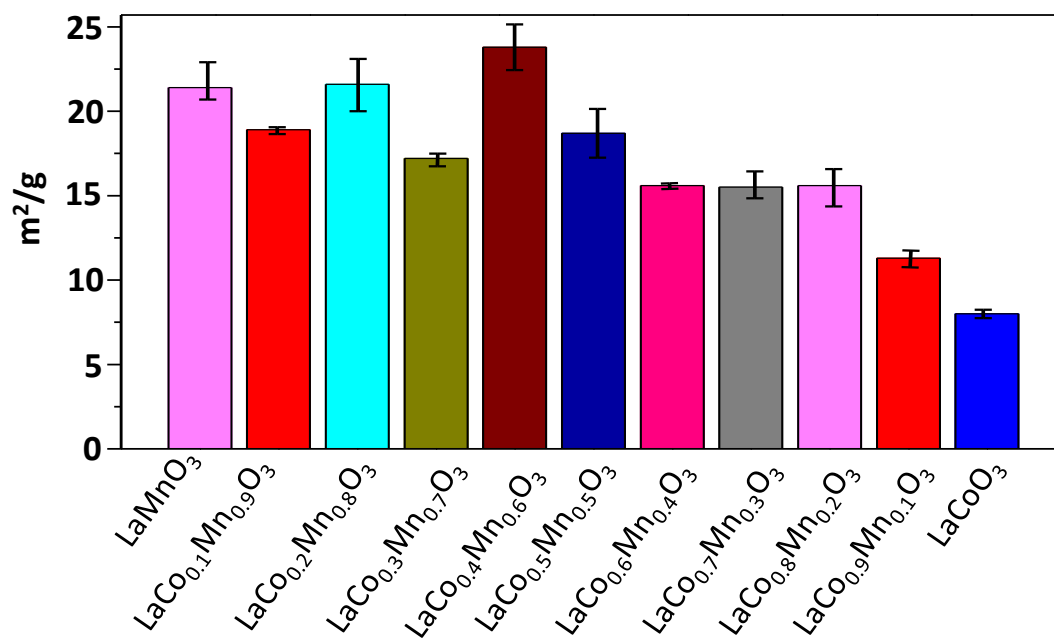
# Appendix

## Appendix A

### Additional Data for Perovskites Based DOC Catalysts



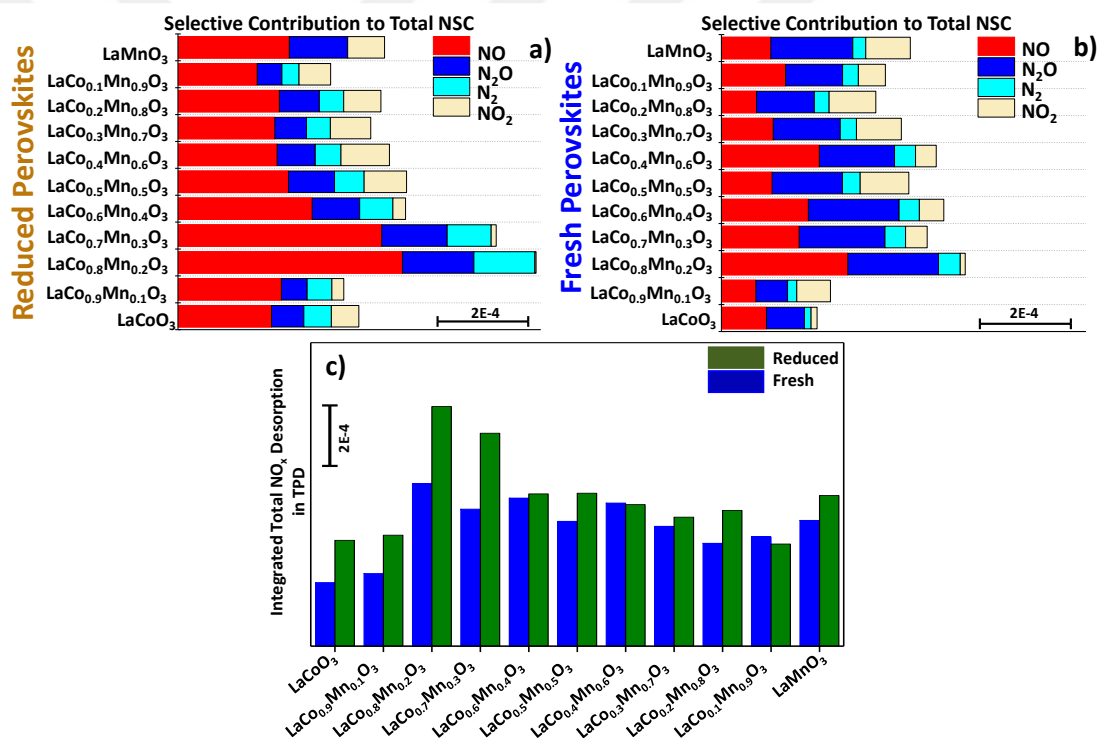
**Appendix A1.** a) Ex-situ XRD patterns in between  $10^\circ < 2\theta < 80$  and b) Detailed crystal structure transformation illustration ( $31^\circ < 2\theta < 35^\circ$ ) of simple  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$  and B-site mixed  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  perovskites ( $0 \leq x \leq 1.0$ ) b) obtained after synthesis and calcination at 973 K.



**Appendix A2.** SSA values of simple  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$  and B-site mixed  $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$  B-site mixed perovskites ( $0 \leq x \leq 1.0$ ).

| Sample                                               | La (ppm) | La % RSD | Mn (ppm) | Mn % RSD | Co (ppm) | Co % RSD |
|------------------------------------------------------|----------|----------|----------|----------|----------|----------|
| LaCoO <sub>3</sub>                                   | 4.18     | <1.0     |          |          | 1.81     | <1.0     |
| LaCoO <sub>3</sub>                                   | 4.27     | <1.0     |          |          | 1.88     | <1.0     |
| LaMnO <sub>3</sub>                                   | 4.17     | <1.0     | 1.69     | <1.0     |          |          |
| LaMnO <sub>3</sub>                                   | 4.25     | <1.0     | 1.75     | <1.0     |          |          |
| LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub> | 4.95     | <1.0     | 0.58     | <1.0     | 1.34     | <1.0     |
| LaCo <sub>0.7</sub> Mn <sub>0.3</sub> O <sub>3</sub> | 5.04     | <1.0     | 0.60     | <1.0     | 1.39     | <1.0     |
| LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub> | 5.18     | <1.0     | 0.46     | <1.0     | 1.62     | <1.0     |
| LaCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>3</sub> | 5.27     | <1.0     | 0.48     | <1.0     | 1.68     | <1.0     |

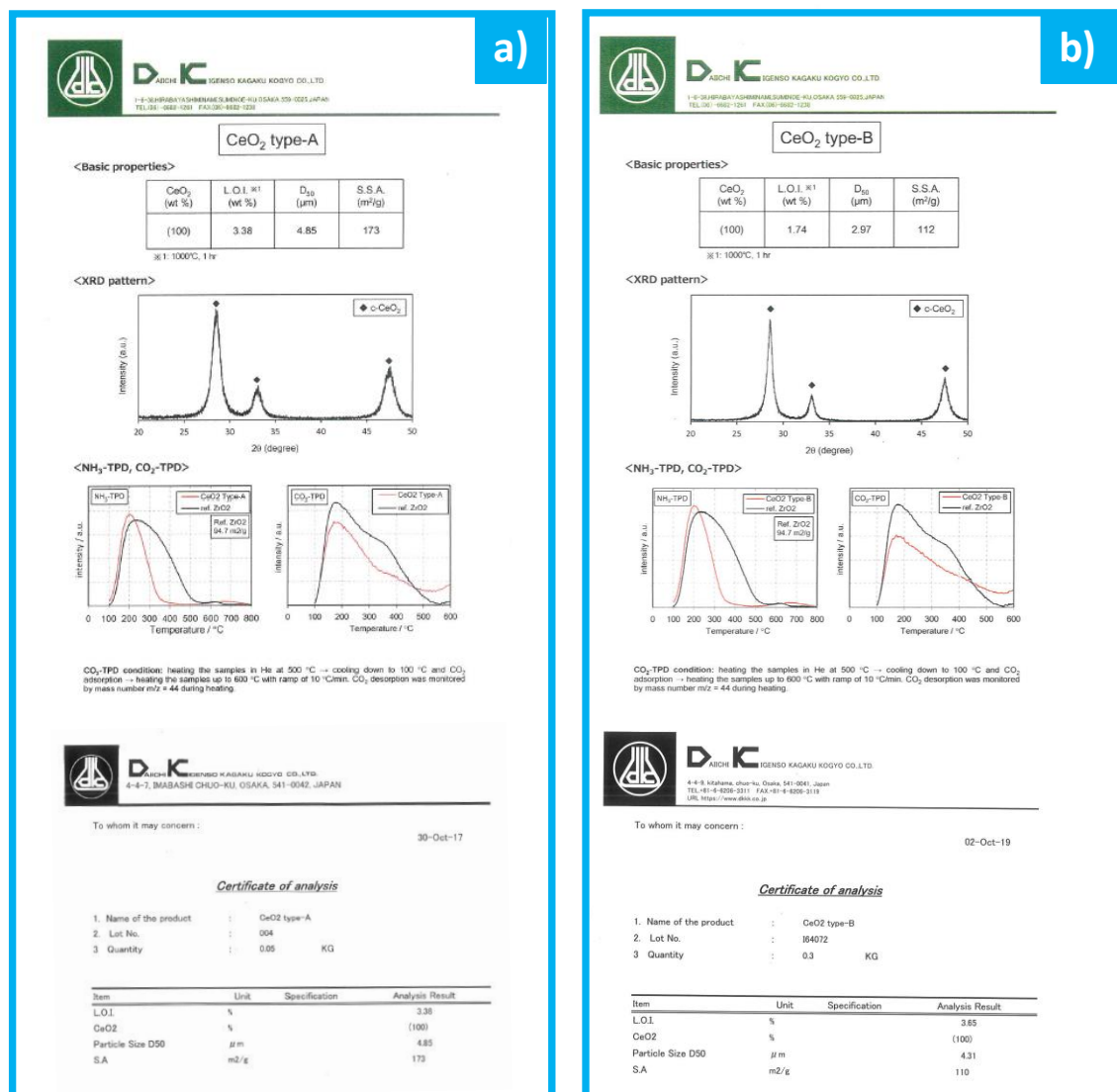
**Appendix A3.** Bulk composition analysis of perovskites via ICP-MS. For each perovskite type, two independent samples were taken and each sample was measured for 5 times. Reported values are mean values of these 5 measurements along with their percent relative standard deviations (RSD %).



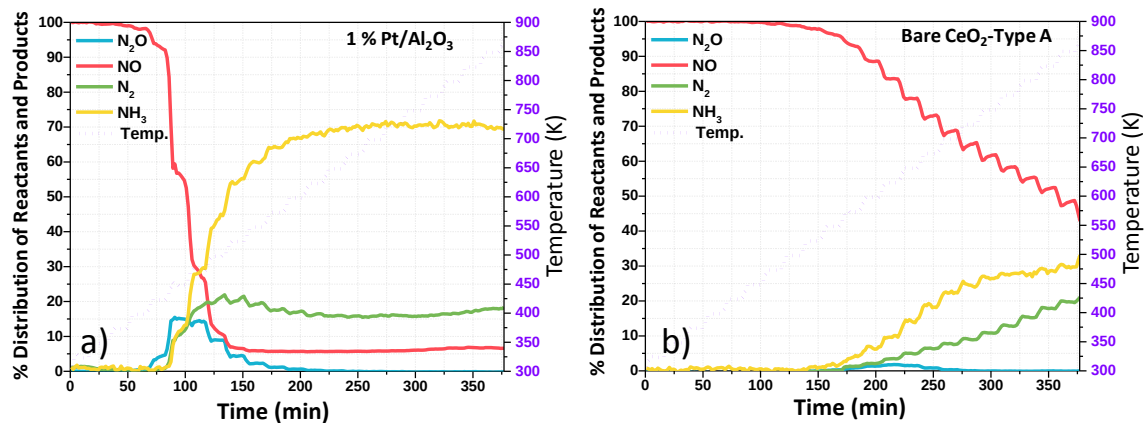
**Appendix A4.** Quantification of the relative QMS intensities of all desorbing species for all of the synthesized perovskites, which were calculated by using mass spectroscopic fragmentation coefficients of all desorbing NO<sub>x</sub> species (i.e., NO<sub>2</sub>, NO, N<sub>2</sub>, N<sub>2</sub>O) in TPD for (a) reduced and (b) fresh samples. (c) Total number of stored NO<sub>x</sub> species (i.e., sum of corrected NO<sub>2</sub>, NO, N<sub>2</sub>, N<sub>2</sub>O TPD signals), obtained from panels (a) and (b).

## Appendix B

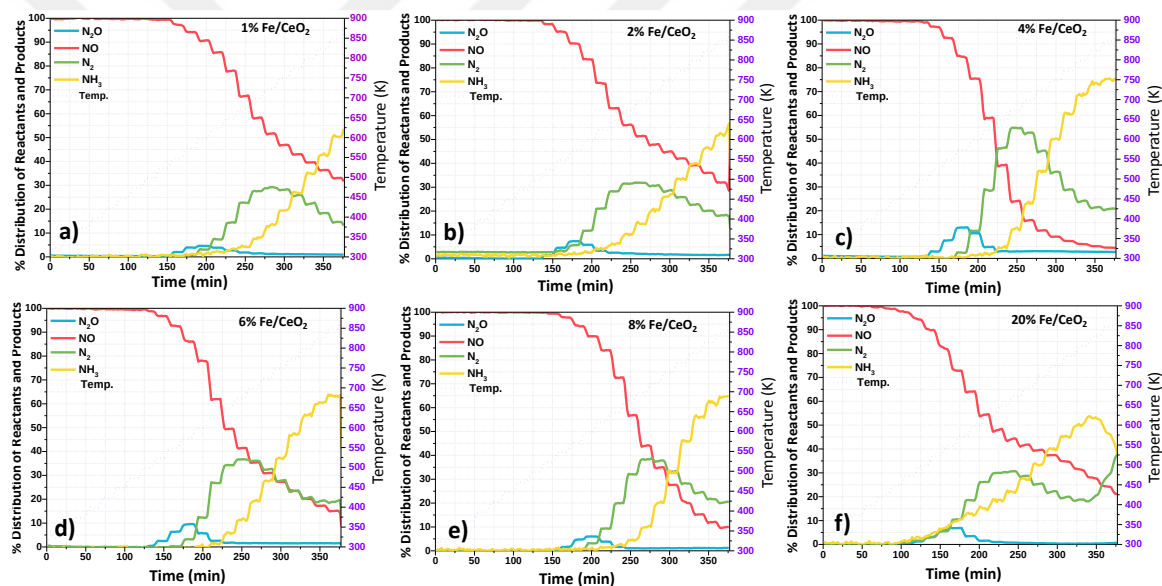
### Additional Data Fe/Co Based and CeO<sub>2</sub> Supported SCR Catalysts



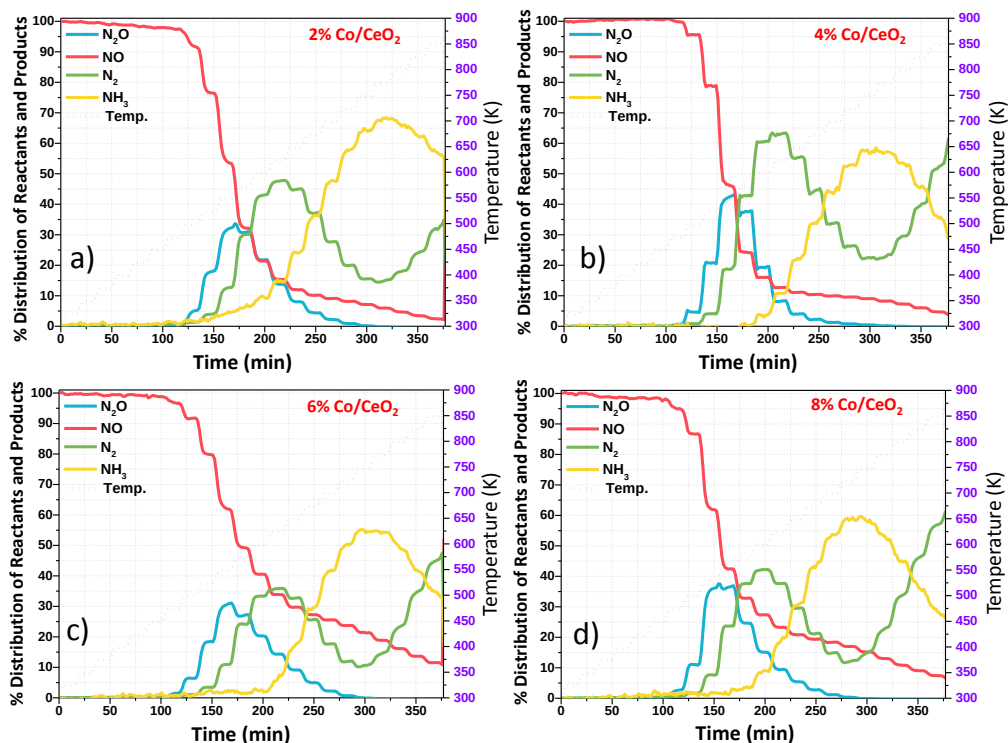
**Appendix B1.** The certification of CeO<sub>2</sub> Type A and Type B provided by DKKK Inc.



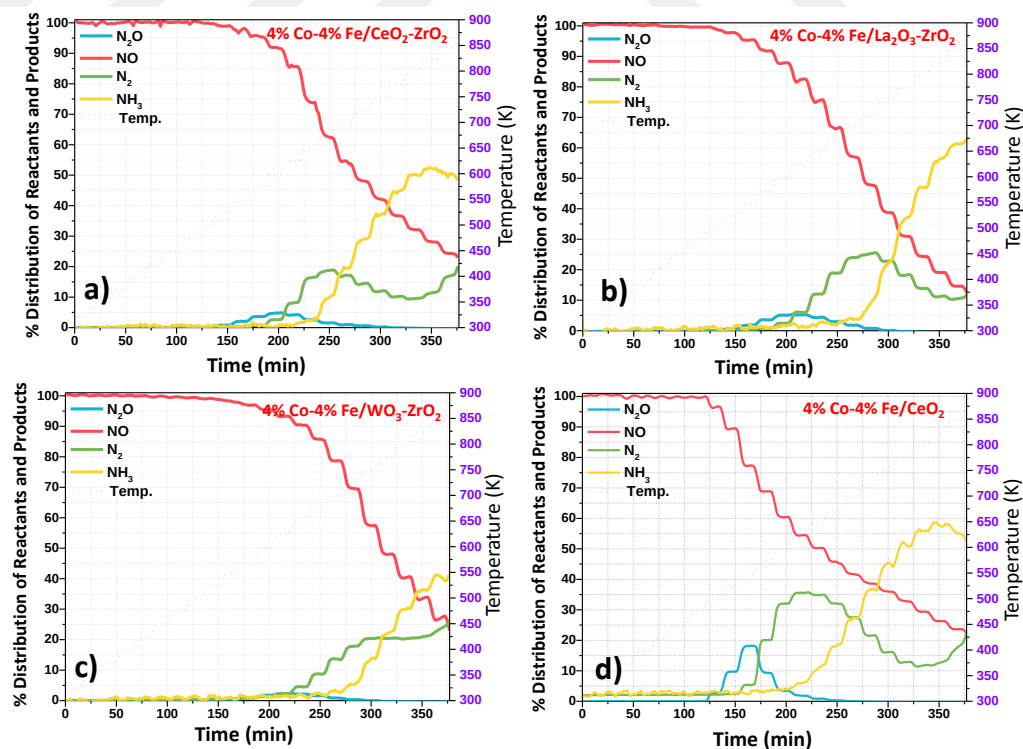
**Appendix B2.** Flow-mode NO reduction experiment results for benchmark catalysts a) 1 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> and b) Bare CeO<sub>2</sub> Type A.



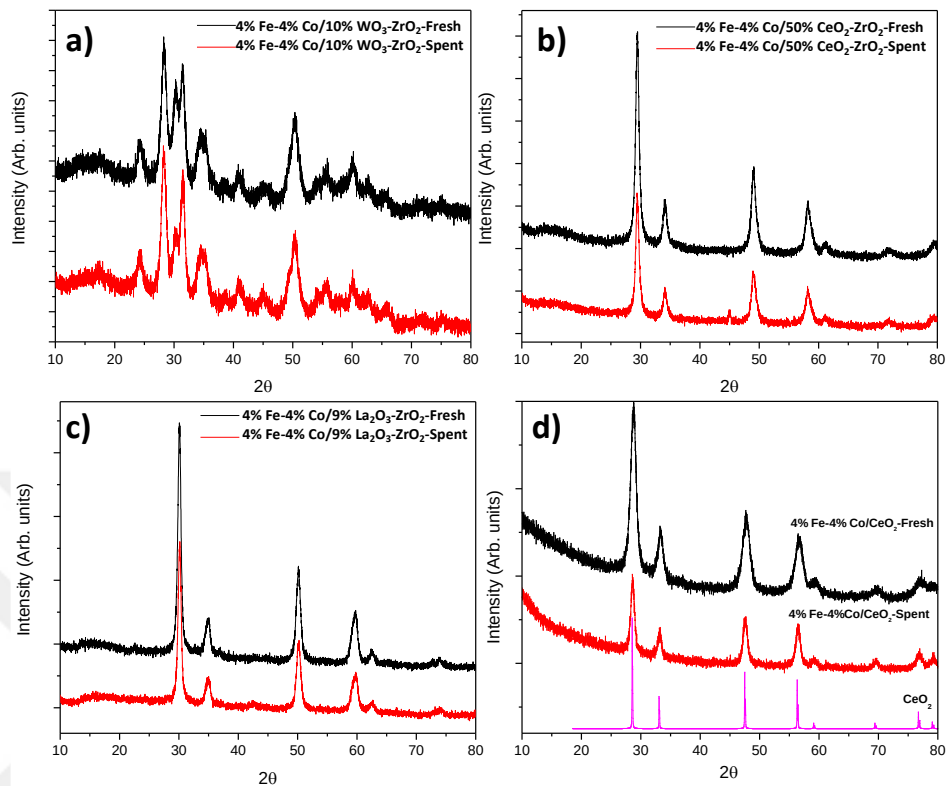
**Appendix B3.** (a-f) Flow-mode NO reduction experiment results for various Fe loadings of 1 to 20 wt. % on CeO<sub>2</sub>.



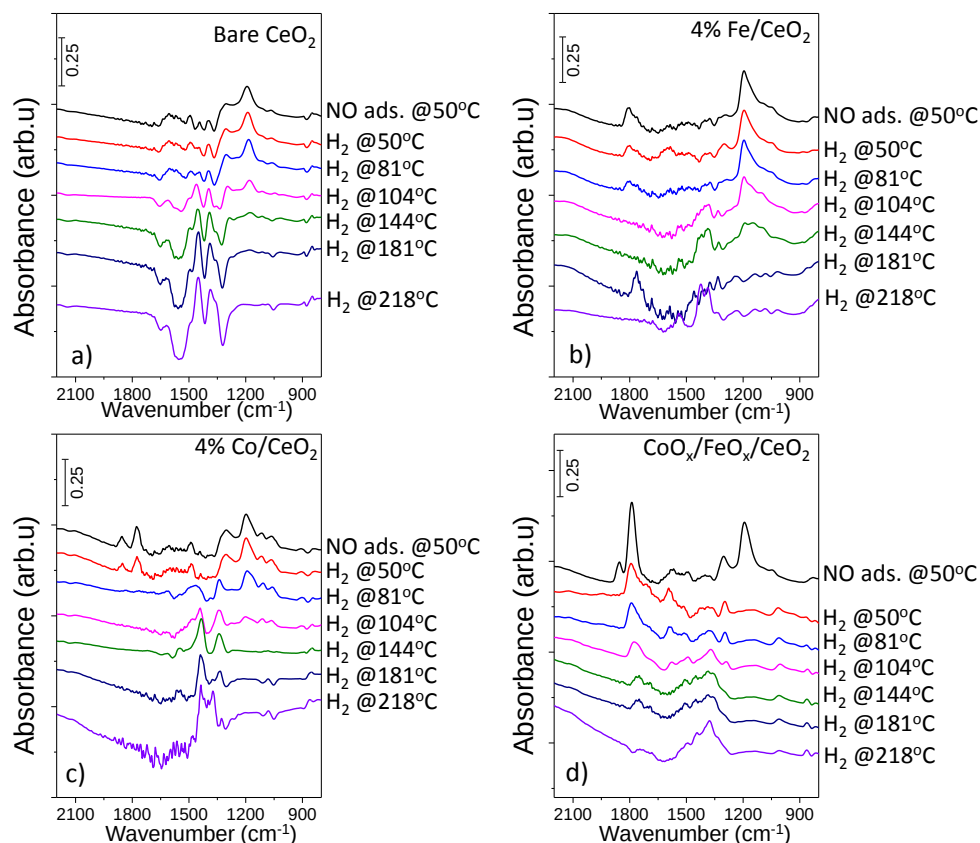
**Appendix B4.** (a-d) Flow-mode NO reduction experiment results for various Co loadings of 2 to 8 wt. % on  $\text{CeO}_2$ .



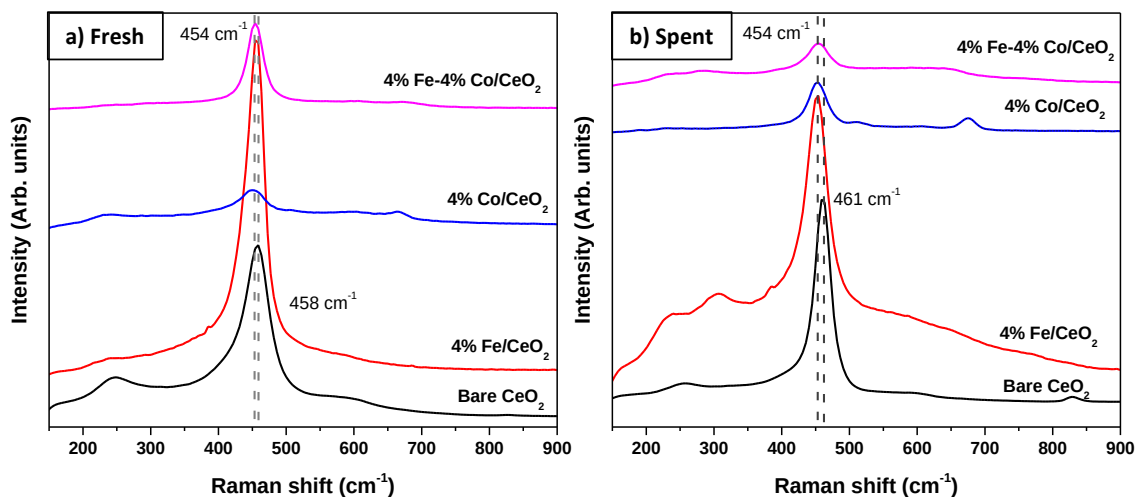
**Appendix B5.** Flow-mode NO reduction experiment results for 4 wt. % Fe-4 wt. % Co loaded on various support materials: a) 50 wt. %  $\text{CeO}_2$ -ZrO<sub>2</sub>, b) 9 wt. %  $\text{La}_2\text{O}_3$ -ZrO<sub>2</sub>, c) 10 wt. %  $\text{WO}_3$ -ZrO<sub>2</sub>, and d)  $\text{CeO}_2$  shown in a to d panels wrt support type.



**Appendix B6.** The comparative fresh and spent XRD profiles for 4 wt. % Fe-4 wt. % Co loaded on a) 10 wt. % WO<sub>3</sub>-ZrO<sub>2</sub>, b) 50 wt. % CeO<sub>2</sub>-ZrO<sub>2</sub> c) 9 wt. % La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, and d) CeO<sub>2</sub>.



**Appendix B7.** In-situ NO adsorption at RT and reduction at various temperatures on a) Bare CeO<sub>2</sub>, b) 4 wt. % Fe/CeO<sub>2</sub>, c) 4 wt. % Co/CeO<sub>2</sub>, and d) 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub>.

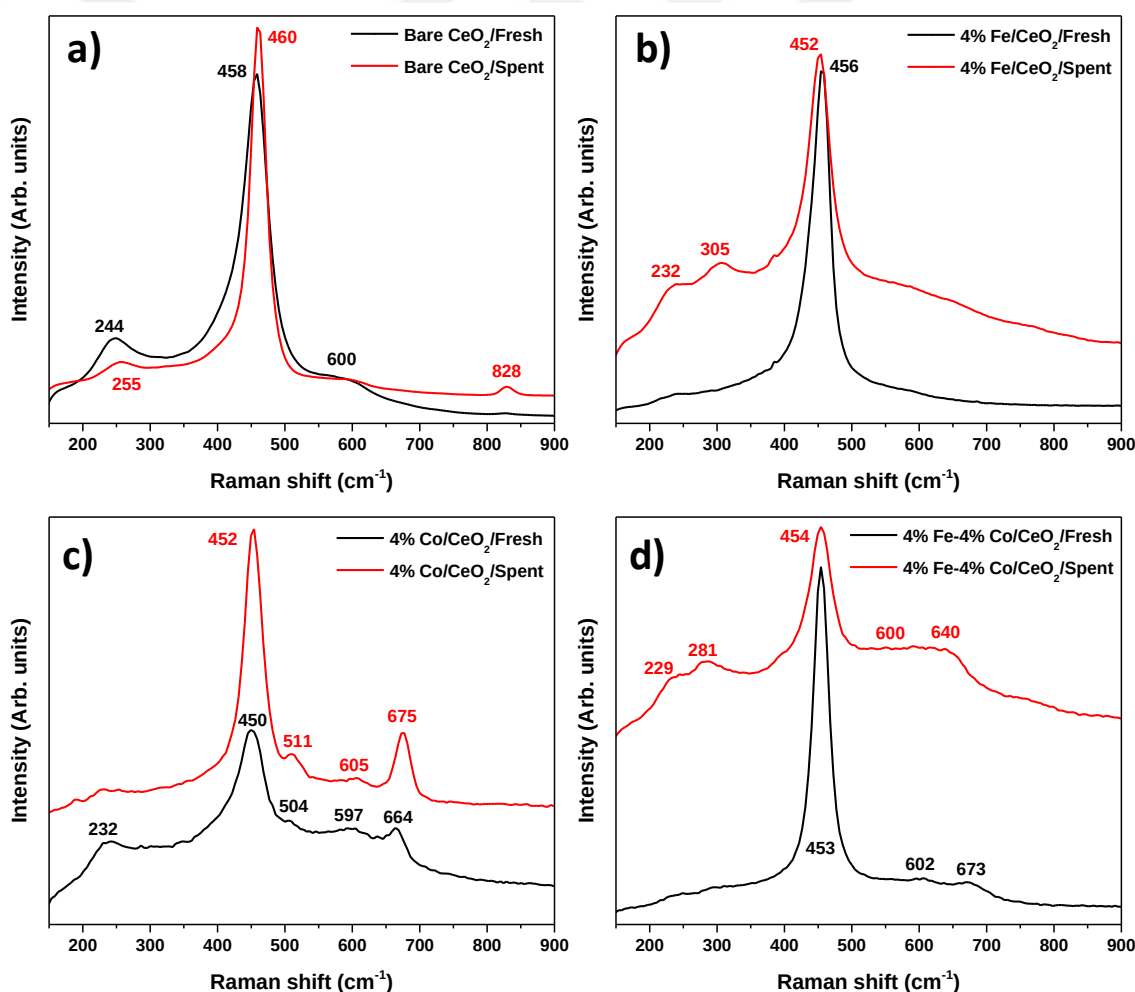


**Appendix B8.** Ex-situ Raman spectra for a) Fresh and b) Spent (recovered catalyst just after NO(g)/H<sub>2</sub>(g) = 1/3 within 300-850 K reaction) Bare CeO<sub>2</sub>, 4 wt. % Fe/CeO<sub>2</sub>, 4 wt. % Co/CeO<sub>2</sub>, and 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub>.

The Raman spectroscopic results for Bare CeO<sub>2</sub>, 4 wt. % Fe/CeO<sub>2</sub>, 4 wt. % Co/CeO<sub>2</sub>, and 4 wt. % Fe-4 wt. % Co/CeO<sub>2</sub> samples are given in **Appendix B8**. The CeO<sub>2</sub> has a well-known characteristic peak observed at around 464-466 cm<sup>-1</sup> that is assigned to F<sub>2g</sub> Raman

mode of fluorite  $\text{CeO}_2$  [114], [117], [284], [285]. For Bare  $\text{CeO}_2$ , this peak is observed at  $458\text{ cm}^{-1}$  which can slightly shift as a function of the degree of crystallinity and particle size [286].

Raman features below  $650\text{ cm}^{-1}$  can be associated with D modes due to disorders such as oxygen vacancies and S modes due to the surface phonons of  $\text{CeO}_2$  [117], [285], [286]. D modes can appear as a result of intrinsic vacancies and metal doping into the ceria lattice [286]. Incorporation of metal cations with a lower oxidation state than  $\text{Ce}^{4+}$  affects the force constant between Ce-O bonds leading to a red shift of the  $\text{F}_{2g}$  mode of ceria [285].



**Appendix B9.** Ex-situ Raman results for fresh and spent (recovered catalyst just after  $\text{NO}(\text{g})/\text{H}_2(\text{g}) = 1/3$  within 300-850 K reaction) a) bare  $\text{CeO}_2$ , b) 4 wt. % Fe/ $\text{CeO}_2$ , c) 4 wt. % Co/ $\text{CeO}_2$ , and d) 4 wt. % Fe-4 wt. % Co/ $\text{CeO}_2$ .

The alteration of Raman features for fresh and spent samples are shown in **Appendix B9** for selected catalysts and for the bare ceria support material. The Raman bands observed

at 244 and 255  $\text{cm}^{-1}$  are ascribed to the nanocrystallized  $\text{CeO}_2$  [285]. The shift and intensity attenuation of 244  $\text{cm}^{-1}$  feature along with the weakening of the D mode at 600  $\text{cm}^{-1}$  for spent bare  $\text{CeO}_2$  (**Appendix B9a**) could be attributed to the healing (filling) of oxygen vacancies of  $\text{CeO}_2$ . However, it is hard to depict a similar conclusion for  $\text{FeO}_x/\text{CoO}_x$  loaded catalysts since  $\text{FeO}_x/\text{CoO}_x$  features significantly overlap with cerium oxide features. Furthermore, appearance of a feature at 828  $\text{cm}^{-1}$  (**Appendix B9a**) is due to the formation of superoxide ( $\text{O}_2^-$ ) species on ceria [287].

4 wt. %  $\text{Fe}/\text{CeO}_2$  sample (**Appendix B9b**) shows a weak signal around 200-300  $\text{cm}^{-1}$  which evolved into two distinctly visible signals at 232  $\text{cm}^{-1}$  and 305  $\text{cm}^{-1}$  after NO reduction. These peaks can be related to small, disordered microcrystals of  $\text{Fe}_2\text{O}_3$  [117]. Characteristic Raman bands of  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  are not clearly observed, which are expected to appear at 650  $\text{cm}^{-1}$  and 670  $\text{cm}^{-1}$ , respectively [117]. Yet, a weak and broad shoulder at ca. 650  $\text{cm}^{-1}$  indicates that presence of  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  as minority species cannot be ruled out entirely.  $\text{F}_{2g}$  signal also exhibits a 4  $\text{cm}^{-1}$  red shift in the spent catalyst as compared to its fresh counterpart which can be due to  $\text{CeO}_2$  reduction or incorporation of other metals (*i.e.*, Fe or Co) into the  $\text{CeO}_2$  lattice after NO reduction [285].

The bands observed for 4 wt. %  $\text{Co}/\text{CeO}_2$  between 500-700  $\text{cm}^{-1}$  and at 232  $\text{cm}^{-1}$  (**Appendix B9c**) can be attributed to  $\text{Co}_3\text{O}_4$  microcrystal formation [117] which become more pronounced for the spent catalyst except the Raman band located at 232  $\text{cm}^{-1}$ . Additionally, narrowing and blue shifting of the fresh catalyst signal at 452  $\text{cm}^{-1}$  in its spent counterpart catalyst can be due to the crystallite size enlargement upon reduction of  $\text{CeO}_2$  [285], [286]. These observations are in line with the presence of the strong evidence for Strong Metal Support Interaction (SMSI) and formation of novel Ce-O-Co sites.

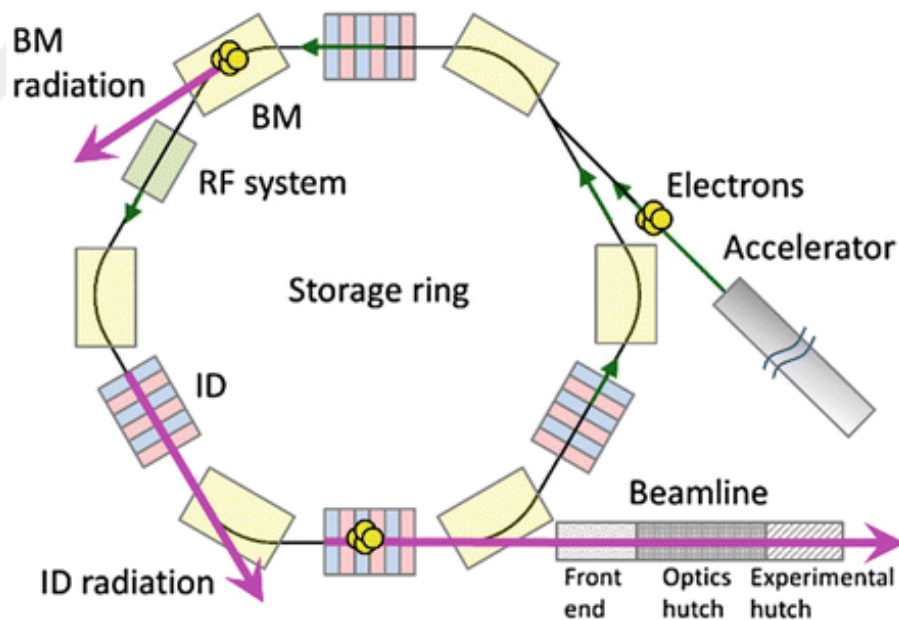
The Raman features of 4 wt. %  $\text{Fe}$ -4 wt. %  $\text{Co}/\text{CeO}_2$  catalyst (**Appendix B9d**) in between 500 to 700  $\text{cm}^{-1}$  can be ascribed to  $\text{Co}_3\text{O}_4$  microcrystal formation [117]. On the other hand, evolution of 229 and 281  $\text{cm}^{-1}$  signals in the spent catalyst (**Appendix B9d**) is consistent with the formation of disordered microcrystals of  $\text{Fe}_2\text{O}_3$  [117].

## Appendix C

### XAS (X-Ray Absorption Spectroscopy) Theory and Data Analysis

X-Rays are classified as electromagnetic radiations having wavelengths within 0.25 Å to 25 Å. The conventional method for X-ray production involves acceleration/deceleration of electrons in strong force fields. Upon establishment of synchrotron radiation sources (SRSs) generating high brilliance X-rays with tunable energies, X-ray absorption spectroscopy (XAS) has become a popular and an efficient nanomaterial characterization tool [288].

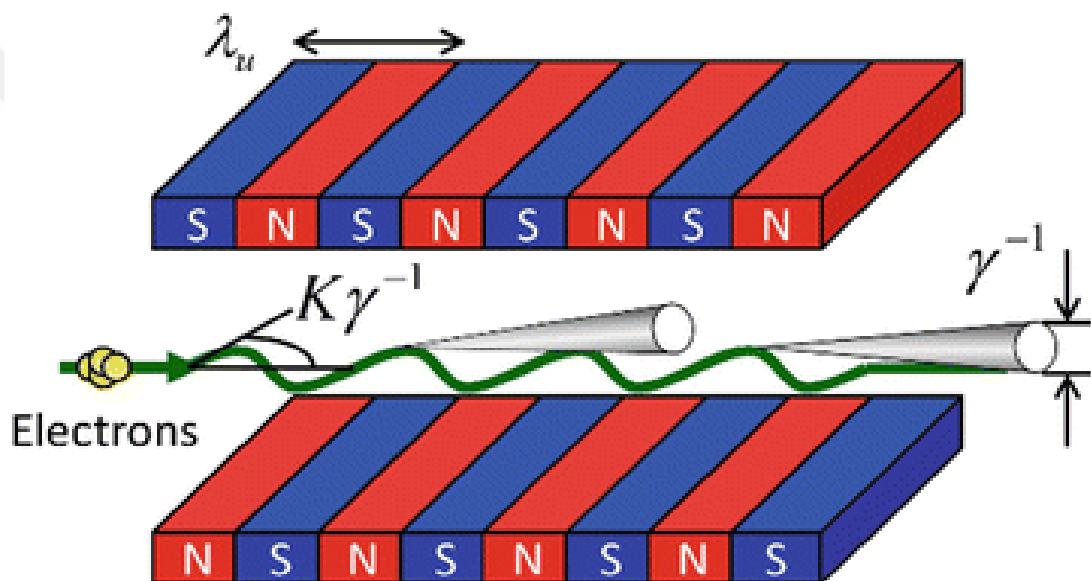
Originally, synchrotrons were built for high-energy physics experiments, but by utilizing electromagnetic radiations (*i.e.*, UV, IR, X-rays) generated by synchrotrons variety of novel experimental methods have been developed as powerful techniques to investigate different materials at the atomic scale.



**Appendix C1.** Operational principle of a typical synchrotron [289]. Copyright (2020) Springer.

The synchrotron-based accelerators are typically comprised of an electron injecting system, a storage ring, bending magnets and/or undulators, optic hutches and experimental hutches (see **Appendix C1**). The circular design of the synchrotrons aims to increase the average lifetime of the accelerated electrons. The operational principle of the synchrotrons can be summarized as follows: firstly, electrons accelerated by the linear accelerator (linac) are

injected into a circular evacuated pipe (storage ring with a base pressure of ca.  $5 \times 10^{-11}$  Torr) which may have 100-1000 m closed path length with bending magnets located at certain points of the ring [290]. Bending magnets (BM) applying Lorentz force perpendicular to propagation direction of electrons lead to the emission of electromagnetic waves called synchrotron radiation (SR) light. Another apparatus to generate emission of light in SR is the Insertion Device (ID) (also called wiggler) in which linearly aligned arrays of magnets (see **Appendix C2**) establishing a unique magnetic field resulting in wiggle movement of electrons due to recurrent magnetic field along ID.

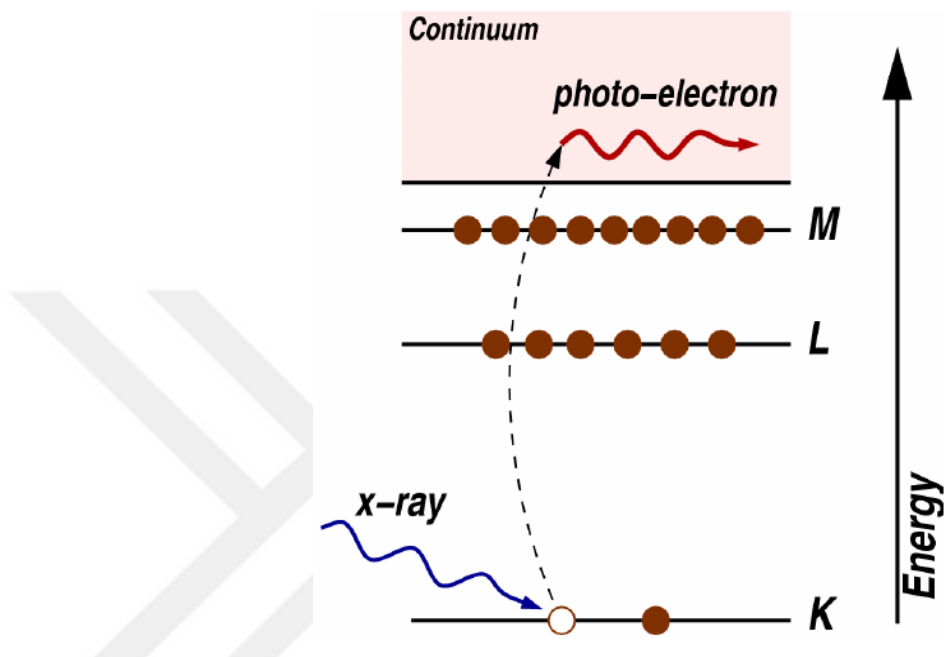


**Appendix C2.** Acceleration of electrons in a magnetic array of an insertion device) [289]. Copyright (2020) Springer.

At each BM and ID point, SR is emitted with different characteristics in terms of photon flux, pulse or continues emission *etc.* SR generates extremely intense light beams with a typical photon flux of  $10^9$ - $10^{10}$  photon/sec [290].

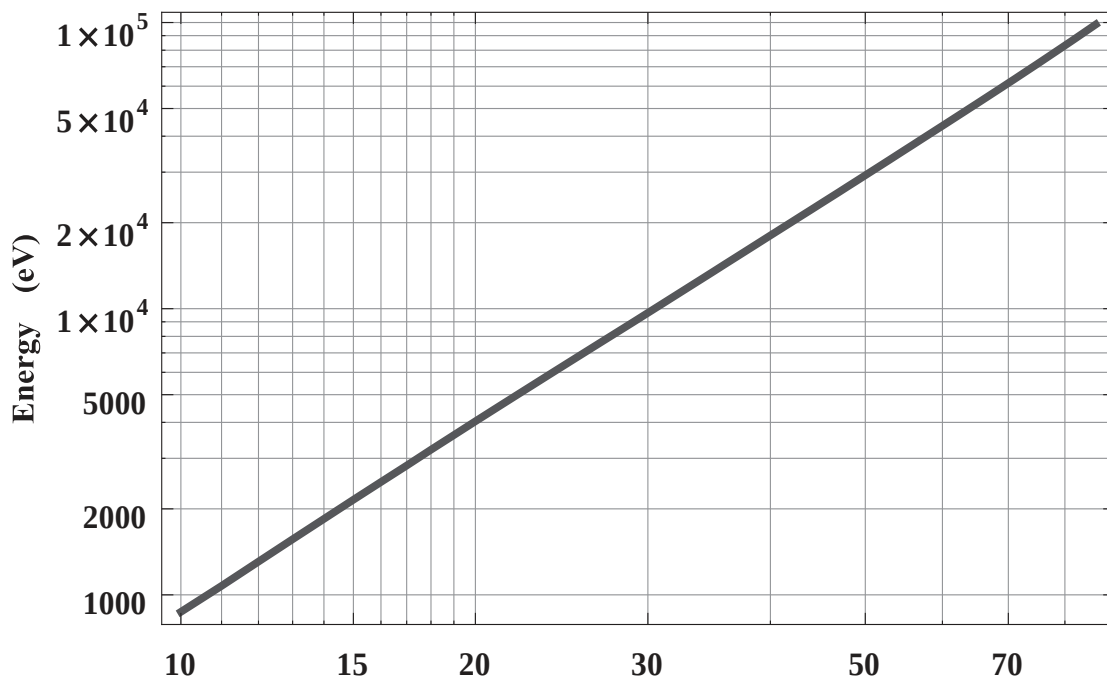
X-ray Absorption Spectroscopy (XAS) is a spectroscopic technique consisting of two different regimes called as X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine-Structure (EXAFS). XANES and EXAFS focus on different energy intervals of the XAS spectrum. XANES is mostly sensitive to valence state and coordination chemistry of the main absorber atom. However, EXAFS provides information on the types of atoms in the closest neighboring of the absorbing atom, atomic distances and coordination numbers of the main absorber. In SR, energy of X-ray photons

can be typically varied in between 500 eV to 500 keV (corresponding to DeBroglie wavelengths of 0.25 Å to 25 Å, respectively). Core electrons of the absorbing atom can be excited to continuum by X-ray absorption with sufficient energy (see **Appendix C3**) [291].



**Appendix C3.** The schematic demonstration of photo electric effect excitation of core level electron to continuum level [292]. Copyright (2020) Mineralogical Society of America.

Due to spin orbit coupling ( $J = L + S$ , where  $J$  is total angular momentum,  $L$  is total orbital angular momentum and  $S$  is the total spin angular momentum), for orbital quantum numbers  $\geq 1$  (i.e.,  $l \geq 1$ ) splitting of the absorption lines are observed. Hence, X-ray absorption lines due to core level electrons can be assigned using the following notation: 1s (K), 2s ( $L_1$ ), 2p<sub>1/2</sub> ( $L_2$ ), 2p<sub>3/2</sub> ( $L_3$ ), 3s ( $M_1$ ), 3p<sub>1/2</sub> ( $M_2$ ), 3p<sub>3/2</sub> ( $M_3$ ), 3d<sub>3/2</sub> ( $M_4$ ), and 3d<sub>5/2</sub> ( $M_5$ ). When the incident x-ray beam has an energy just enough to excite a particular type of core electrons, a dramatic increase in the absorption of X-rays by the atom is observed which is called the “absorption edge” (e.g., K-edge,  $L_1$ -edge etc.). Absorption edges of most of the common elements appear within 5 to 35 keV.



**Appendix C4.** Logarithmic plot of K-edge energies as a function of atomic number (Z) [290], [293] copyright (2020) Wiley), respectively.

**Appendix C4** shows K-edge energy variation as a function of the atomic number  $Z$  of the absorbing atom where the edge energy follows an empirical relationship of  $Z^{2.16}$  [290]. In EXAFS studies, extent of X-ray absorption as a function of incident beam energy (*i.e.*,  $\mu(E)$  = absorption coefficient) is measured.  $\mu(E)$  can be considered as the absorption probability of X-rays based on Beer's Law:

$$I = I_0 e^{-\mu t} \quad A-1$$

Where  $I$  is transmitted x-ray intensity,  $I_0$  is the intensity of the incoming x-rays and  $t$  is the thickness of the sample.



**Appendix C5.** The schematic illustration of transmission-based EXAFS experiments [290]. Copyright (2020) Wiley.

Measurement of the ratio between  $I$  and  $I_0$  (see **Appendix C5**) allows determination of the absorption coefficient,  $\mu(E)$ . Typical design of the X-ray transmission experiments requires SR (X-ray source), monochromator (energy selection), and ionization detectors (measures

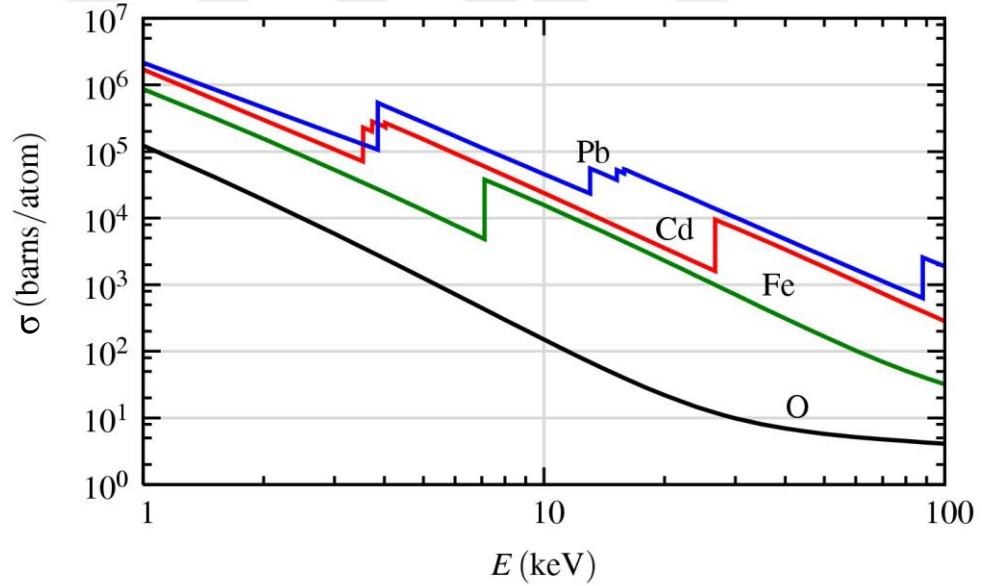
$I/I_0$  ratio). On the other hand,  $\mu(E)$  also depends on the density of the sample ( $\rho$ ), atomic mass ( $A$ ), X-ray energy ( $E$ ) and atomic number ( $Z$ ) as follows:

$$\mu \approx \frac{\rho Z^4}{AE^3} \quad A-2$$

Additionally, the absorption coefficient can be written as a function of density of sample ( $\rho$ ) and X-ray absorption cross section ( $\sigma$ ) as:

$$\mu = \rho \cdot \sigma \quad A-3$$

**Appendix C6** shows the absorption cross section variation as a function of absorbed X-ray energies for selected elements. Due to significant differences in the atomic numbers of Pb, Cd, Fe, and O, these elements reveal quite dissimilar  $\sigma$  values. Thus,  $\sigma$  values can often be used as a characteristic indicator to identify a particular element. The sudden jumps in  $\sigma$  values in **Appendix C6** correspond to an edge energy of the given element.

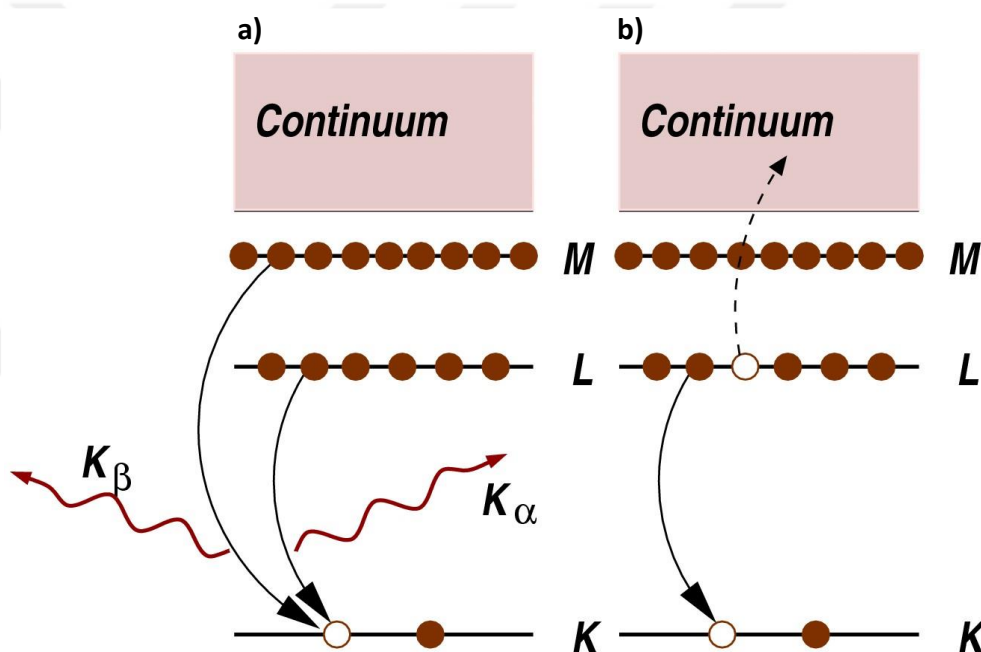


**Appendix C6.** The absorption cross section of selected elements as a function of energy [292]. Copyright (2020) Mineralogical Society of America.

The absorption cross section is also important in the XANES/EXFAS sample preparation as it can be used to adjust concentration/thickness of the sample. In order to avoid insufficient transmission signal of the chosen elements at a given edge energy, it is important to adjust concentration and thickness of the corresponding sample. Furthermore, as can be seen in **Appendix C6** at low energies absorption cross section is very high. Hence,

for heavy elements, it is better to investigate high-energy edges leading to a clear/sharp edge which also precludes signal overlap from other atoms of different atoms present in the sample.

In order to circumvent the insufficient signals in transmission-mode XAS due to high absorption cross section restrictions, fluorescence or total electron yield methods could be utilized to obtain reasonable signals. Upon excitation of an electron from the consistent shell, two major atomic relaxation pathways are commonly observed, which are X-ray fluorescence and Auger electron emission processes (see **Appendix C7**).

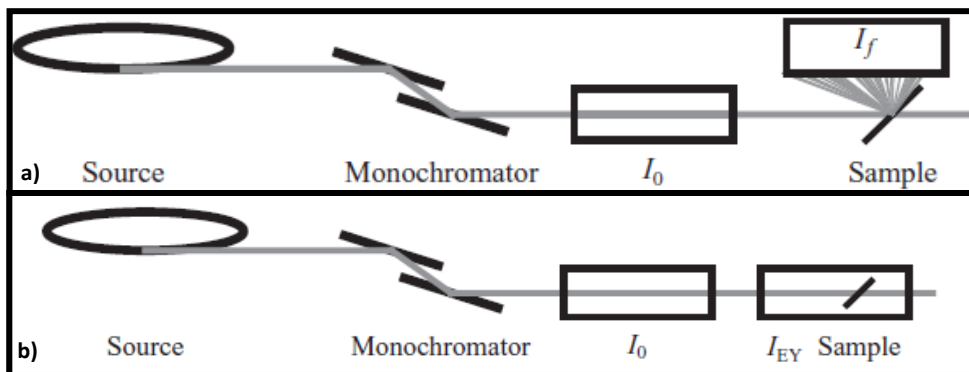


**Appendix C7.** The excited state emission either as (a) fluorescence or (b) Auger electron emission [292]. Copyright (2020) Mineralogical Society of America.

By positioning an appropriate detector after the sample, both methods can be used to analyze the samples for XAFS experiments. The main advantage of using fluorescence or total electron yield methods is to be able to analyze thin samples with low concentrations. The dependence of  $\mu(E)$  to fluorescence or Auger emission can be expressed as:

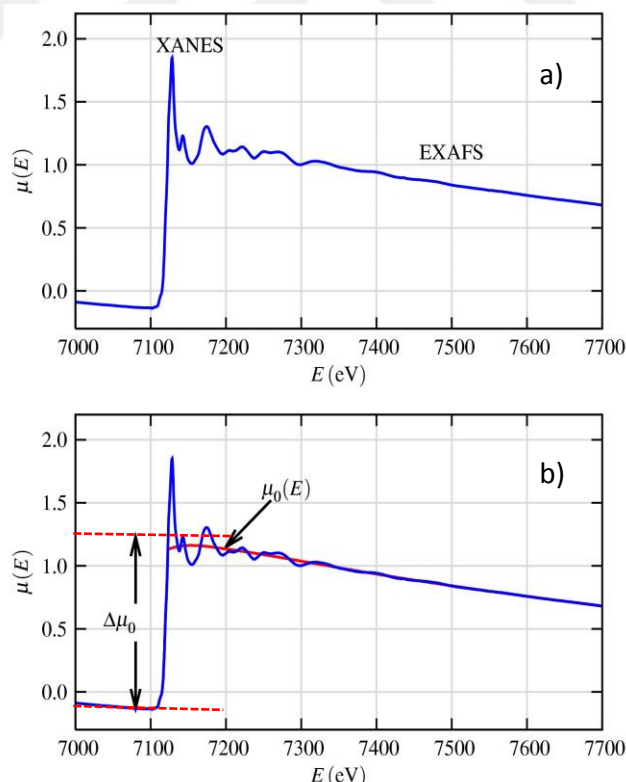
$$\mu(E) \propto I_{f \text{ or } I_{EY}}/I_0 \quad \text{A- 4}$$

The  $I_f$  is the intensity of fluorescent photons and  $I_{EY}$  is the electron yield intensity, and  $I_0$  is the intensity of the incoming X-rays.



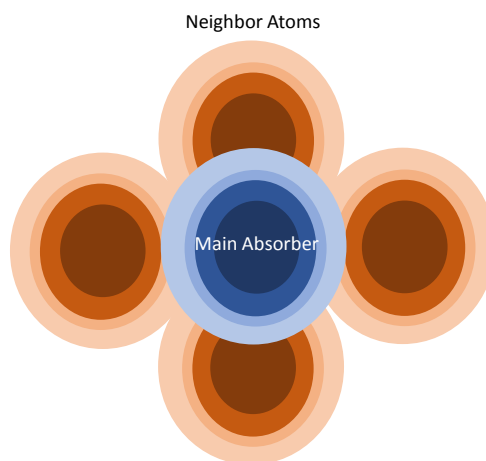
**Appendix C8.** Illustration of a) florescence and b) electron yield configurations for XAFS experiments. Adapted from Ref [290] Copyright (2020) Wiley.

**Appendix C8** illustrates two different experimental configurations for the florescence and total electron yield modes of XANES/EXAFS measurements. In XAFS experiments, the major parameter measured is  $\mu(E)$  as it is directly used in the mathematical data analysis to deduce chemical, structural and electronic properties of the absorbing atom and the neighboring atoms.



**Appendix C9.** XAS spectra of FeO: a) XANES and EXAFS regions, b) edge step ( $\Delta\mu_0$ ) [292]. Copyright (2020) Mineralogical Society of America.

**Appendix C9** depicts a typical XAS spectrum indicating XANES and EXAFS regions. The XANES region is located before the absorption edge rise (**Appendix C9a**) and ends just after first absorption peak. The sharp rise at the edge called the “white line” where edge energy ( $E_0$ ) is defined as the inflection point of the absorption coefficient at the edge step.  $E_0$  is typically positioned close to the middle of the white line. On the other hand, EXAFS region is located immediately after the edge step and contains oscillations, which fade monotonically with increasing energy. In addition, extended absorption of the main absorber atom without the effect of other atoms can be estimated as the  $\mu_o(E)$  curve which is also shown in **Appendix C9b**. In the XAFS experiments, two distinct phenomena are observed, the first one is the photoelectron generation due to the excitation of the core level electrons and the second one is the backscattering of the photoelectrons from the electrons of neighboring atoms. When the incident x-ray energy exceeds the edge energy, excited electrons gain kinetic energy and back scatter from the neighboring atoms of the main absorber. Therefore, the sharp rise in the XAFS spectrum can be correlated with the electron ejection from the core levels of the main absorber while the oscillations in the spectrum are due to the backscattering of the excited electrons from the neighboring atoms (see **Appendix C10**). Furthermore, these back scattered electrons propagate in the form of spherical waves and may create constructive or destructive interferences depending upon the interatomic distances and number of neighboring atoms.



**Appendix C10.** The spherical wave propagation demonstration of the main absorber and the neighbour atoms.

The path of backscattered electrons is also important for the constructive or destructive interference event generating the EXAFS oscillations. Hence,  $\mu_o(E)$  can be considered as

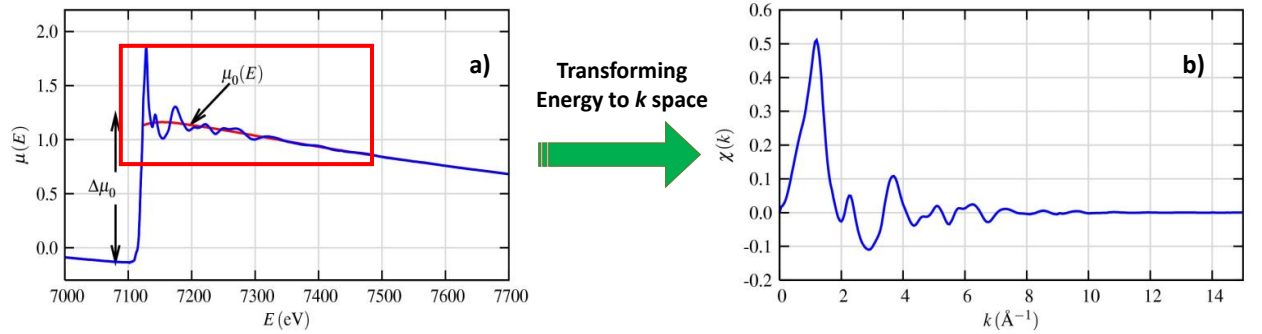
the theoretical estimation of the absorption coefficient free of the backscattering events due to the neighboring atoms [290]. The  $\Delta\mu_0$  (see **Appendix C 9b**) is used for normalization of edge step to 1 which always used for XAS spectra to find out ideal oscillations at edge step at 1. EXAFS oscillations can be mathematically expressed as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0} \quad A-5$$

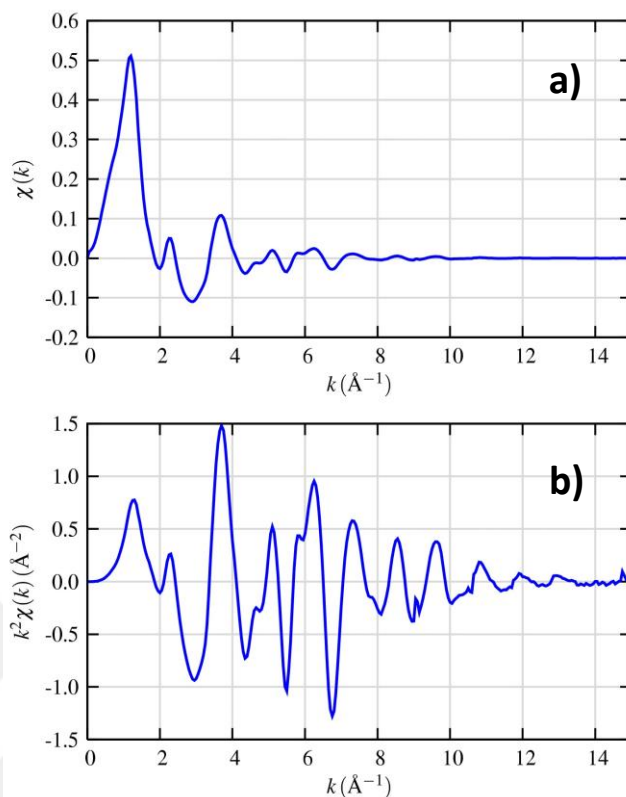
Where  $\chi(E)$  is called the EXAFS function representing the magnitude of the oscillations in the EXAFS region,  $\mu(E)$  is absorption coefficient, and  $\mu_0(E)$  is the background function. Then, the energy oscillations in the extended region  $\chi(E)$  can be converted into to a waveform  $\chi(k)$  (**Appendix C11**), by using the following transformation converting energy into the wavenumber or wave vector ( $k$ ), with units of  $\text{\AA}^{-1}$ :

$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}} \quad A-6$$

In the equation above,  $m$  is the mass of electron,  $\hbar$  is the Planck's constant and  $(E-E_0)$  is the amount of energy exceeding the edge energy.



**Appendix C11.** Illustration for EXAFS data transformation of FeO from a) energy to b)  $k$  space adapted from ref [292]. Copyright (2020) Mineralogical Society of America.

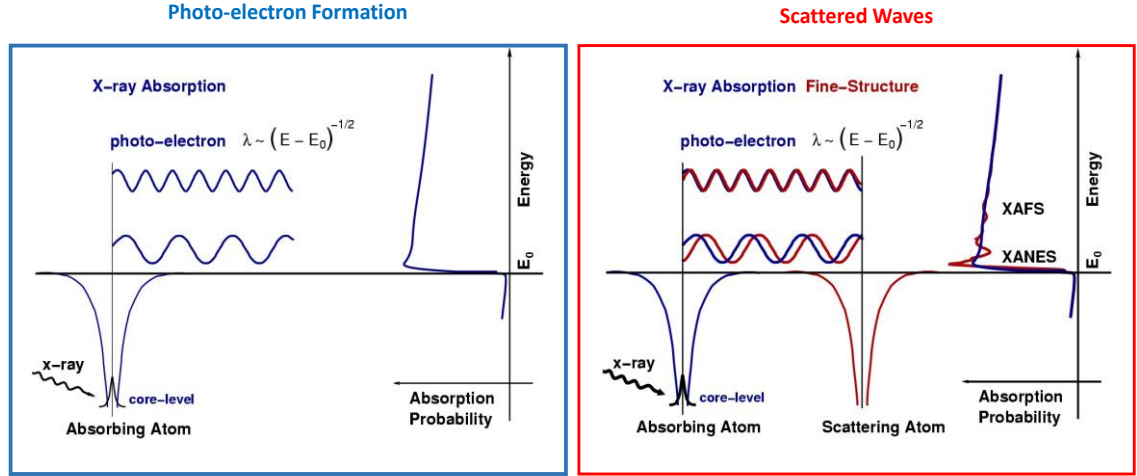


**Appendix C12.** The EXAFS data for FeO a) isolated  $\chi(k)$  and  $k$ -weighted  $k^2\chi(k)(\text{\AA}^{-2})$  demonstration [293]. Copyright (2020) Mineralogical Society of America.

The  $k$ -weighted EXAFS function ( $k^2\chi(k)(\text{\AA}^{-2})$ ) is used to amplify the oscillations at high  $k$  values (**Appendix C12**). The data amplification at high  $k$  values enables extraction of detailed structural information from small oscillations which are not significant in the  $\chi(k)$  curve.

### Development of the EXAFS Equation

Another crucial step is the derivation of EXAFS equation as a function of  $\chi(k)$ . Isolated single atoms have only a sharp increase at  $E_0$ . However, the coordinated species generate oscillations due to the additional scattering events (**Appendix C13**).



**Appendix C13.** The schematic illustration of photo-electron formation from the single atom, scattering of those photo-electrons from the neighbouring atoms and the difference between the isolated and the coordinated atoms due to scattering. Adapted from Ref [292]. Copyright (2020) Mineralogical Society of America.

The Fermi's Golden rule can be used to express  $\mu(E)$  as a transition state between ground (not irritated by x-rays) and excited states (irritated by X-rays) which can be counted as the initial and final quantum states, respectively and it can be expressed as:

$$\mu(E) \sim |\langle i | \mathcal{H} | f \rangle|^2 \quad A-7$$

Where  $\langle i |$  can be defined as the initial quantum state for core electrons and the effect of neighboring atoms is not considered for this state.,  $\mathcal{H}$  is the Hamiltonian and used to define relations between electromagnetic dipole and the electrons (i.e.,  $\mathcal{H} = e^{ikr} \approx 1$ ), while  $|f\rangle$  is defined as the final quantum state which includes photoelectron interaction between the main absorber and neighbor atoms. On the other hand, the final quantum state can be written as:  $|f\rangle = |f_o + \Delta f\rangle$  where  $\Delta f$  is added to express the alteration of the final state of photoelectron due to backscattering. Consequently,  $\mu(E)$  can be written as:

$$\mu(E) \sim |\langle i | \mathcal{H} | f_o \rangle|^2 \left[ 1 + \frac{\langle i | \mathcal{H} | \Delta f \rangle \langle f_o | \mathcal{H} | i \rangle^*}{|\langle i | \mathcal{H} | f_o \rangle|^2} + C. C \right] \quad A-8$$

Based on the equation (A- 5) ,  $\mu(E)$  and  $\chi(E)$  can be expressed as:

$$\mu(E) = \mu_0(E) [1 + \chi(E)] \quad A-9$$

then it follows that  $\chi(E)$  and  $\mu_0(E)$  can be written as:

$$\chi(E) \sim \langle i | \mathcal{H} | \Delta f \rangle \quad A-10$$

$$\mu_0(E) \sim |\langle i | \mathcal{H} | f_o \rangle|^2 \quad A-11$$

The above equations can help us to derive  $\chi$  function. Here, full mathematical of this derivation will be avoided as the main objective of this discussion is to provide a basic understanding of the EXAFS equation and the associated parameters corresponding to physical quantities. The comprehensive understanding of EXAFS equation is critical to analyze the data accurately (especially establishment of the structural models based on the EXAFS data).

By utilizing the equations (A- 10) and (A- 11),  $\chi(k)$  can be written as:

$$\chi(k) = \frac{e^{ikr}}{kr} [2kf(k)e^{i\delta(k)}] \frac{e^{ikr}}{kr} + C. C. \quad A- 12$$

The  $\frac{e^{ikr}}{kr}$  term in the EXAFS equation, represents the spherical wave propagation of the scattering electron from the atom located at a distance  $r$ , and the terms  $f(k)$  and  $\delta(k)$  stand for the amplitude of the scattering from the neighboring atoms and phase shift of the scattered electron, respectively.

By simplifying the complex conjugate terms (C.C.) in equation (A- 12), the EXAFS equation for a single scattering process can be written as (note that  $R$  in equation (A- 13) is equal to the  $r$  in equation (A- 12)):

$$\chi(k) = \frac{f(k)}{kR^2} \sin[2kR + \delta(k)] \quad A- 13$$

Equation (A- 13) demonstrates the magnitude of  $\chi(k)$  just for single scattering, hence multiple scattering effects, number of neighboring atoms (coordination,  $N$ ), thermal/static (or called as Debye-Waller factor) disorder term, the mean free path of the photo-electron, core-hole lifetime, and the relaxation effect of the main absorber are not considered in this equation. The above-mentioned effects are considered separately for the EXAFS equation, which is useful to develop a model for the experimental data.

#### **Neighboring atoms ( $N$ ) and the disorder term contribution ( $\sigma^2$ ):**

The temperature elevation of the sample increases the thermal motion of the atoms. This results in longer scattering paths as compared to the scattering paths at low temperatures. The elongation can be calculated by using vibrational modes and atomic forces of the given lattice. The corresponding eigenvectors and frequencies for a scattering path can be used

to estimate ( $\sigma^2$ ) i.e., the mean square displacement of a bond distance as a function of temperature, also called the Debye-Waller factor or the disorder term [294]. Additionally,  $\sigma^2$  can also be calculated by using an equation of motion [295]. Equation (A- 13) is only valid for single scattering thus, scattering from other paths can be included to the expression by multiplying the equation with the coordination number (N):

$$\chi(k) = \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2} \sin [2kR + \delta(k)] \quad A- 14$$

However, it is important to note that the equation (A- 14) is valid for the same type of scattering paths. In other words, the atoms in the coordination are assumed to be identical atoms which are also located at identical distances from the main absorber atom. However, in realistic cases, positions and types of atoms are not identical thus, in order to address those differences,  $\chi(k)$  can be expressed as:

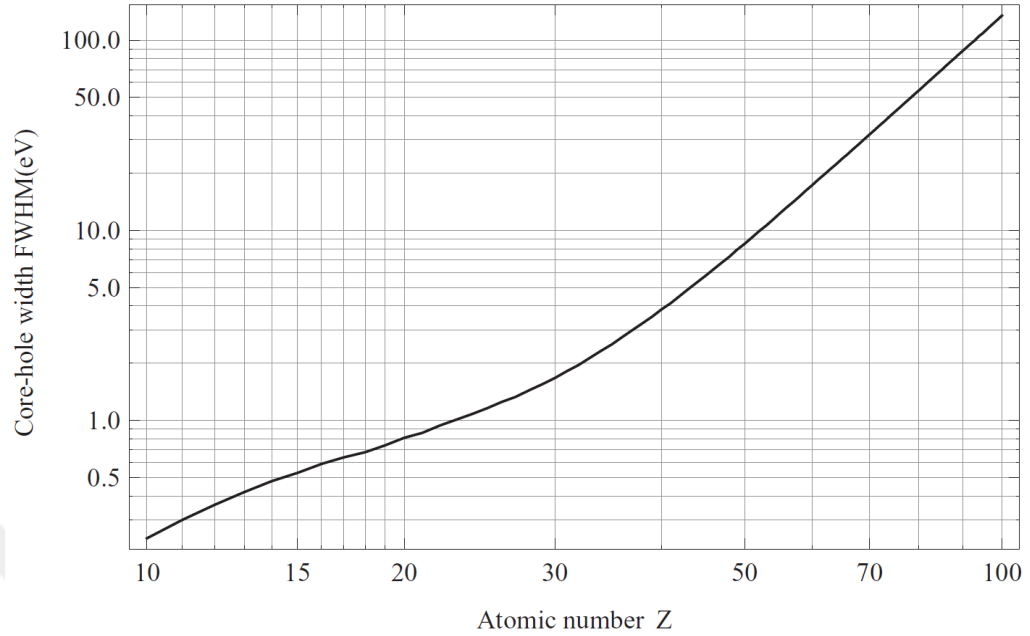
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin [2kR_j + \delta_j(k)] \quad A- 15$$

### **Core-hole lifetime and mean-free path of the photoelectron:**

The core-hole lifetime or core lifetime broadening energy defines energy broadening due to finite energy width of an excited state of the atom. Upon absorption of an x-ray photon with a sufficient energy to excite a core electron generates an electron vacancy (core-hole) in the core energy levels. The energy levels of atoms are normally discrete, and it is assumed that these levels have infinite lifetime, however, the excited atoms are not stable and they have finite lifetime due to non-radiative or radiative relaxation of the excited atom. Thus, based on the Heisenberg uncertainty principle, excited atoms exhibit energy broadening in their lifetime ( $\tau$ ) of this uncertain energy level. The energy broadening can be expressed as in terms of  $\tau$  (lifetime of an excited atom) and  $\hbar$  (Planck's constant divided by  $2\pi$ ):

$$\Delta E \approx \hbar/\tau \quad A- 16$$

The  $\Delta E$  energy broadening declines in accordance with atomic number (Z).



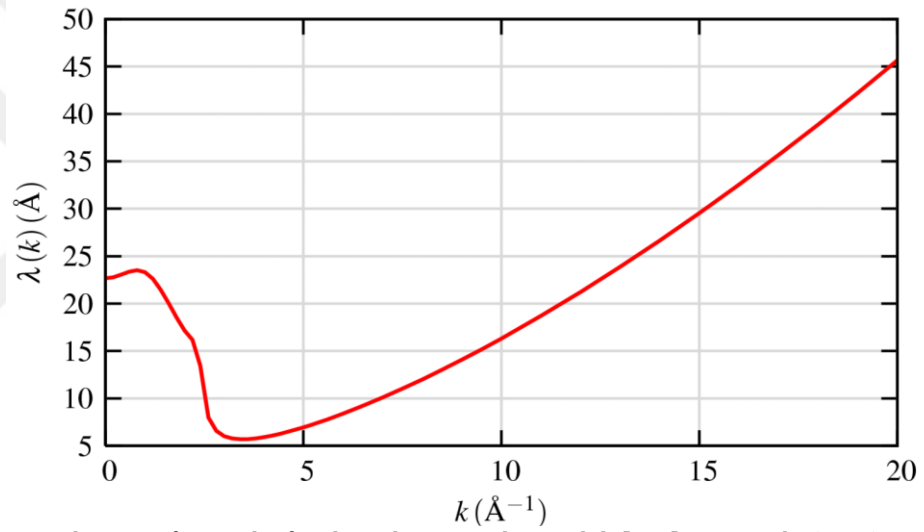
**Appendix C14.** The core-hole width, full width half maximum (FWHM) in response to atomic number (Z) of an excited atom with X-rays. Energy broadening values given above belong to excited level of an atom from the K-edge [290]. Copyright (2020) Wiley.

The core-hole broadening values for K-edge are shown in **Appendix C14**. They reveal a sharp increase especially after  $Z=20$ . This broadening phenomenon should be carefully considered during experimental XANES/EXAFS data acquisition (i.e., while setting the energy scan resolution for XAFS experiments for a given atomic number and a given edge). Additionally, the photoelectron mean free path is another crucial factor that effects EXAFS oscillations. In the previous EXAFS equations, all scatterings were assumed to be elastic scatterings but there is also the possibility that electrons can scatter inelastically. Hence, mean free path,  $\lambda(k)$ , defines the path distance of the photoelectron during the core-hole lifetime until inelastic scatterings become dominant.

The **Appendix C15** shows the mean free path or travel distance of the photoelectron in the lattice as a function of  $k$  or the kinetic energy ( $E-E_0$ ) of the electron. By using damped version of the wave function, EXAFS equation can be expressed as:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)] \quad A-17$$

The above expression includes both core-hole time and mean free path,  $\lambda(k)$  of the photoelectron and the frequency of EXAFS oscillations. By simultaneous utilization of the  $\lambda < 30 \text{ \AA}$  and  $R^2$  in the denominator, the highest travel distance of a photoelectron can be constrained as  $5 \text{ \AA}$ . This makes EXAFS only sensitive to the local structure of the x-ray absorbing atom [292]. It is also important to discuss the coordination sphere concept in the EXAFS data. The atoms with the closest distance to the main absorber can be identified as the atoms in the 1<sup>st</sup> coordination shell. As the coordination sphere is propagated, 2<sup>nd</sup> and 3<sup>rd</sup> coordination shells come into play which are restricted to  $5 \text{ \AA}$  distance due to finite mean-free path of the photoelectron.



**Appendix C15.** The mean free path of a photoelectron in line with  $k$  [292]. Copyright (2020) Mineralogical Society of America.

### The contribution of the $S_0^2$ (amplitude reduction factor):

Considering the probability of multiple excitation events (*i.e.*, shake-up and shake-off processes) of the passive electrons in the x-ray absorber atom [296], the amplitude of the EXAFS oscillations in the finite structure may be modified. Therefore, theoretical/experimental amplitude reduction factors ( $S_0^2$ ) are used to alter the EXAFS equation, where the amplitude reduction factor typically acquires values within  $0.7 < S_0^2 < 1.0$ . The modified version of the EXAFS equation can be written as:

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)] \quad A-18$$

The equation (A- 18) is the final form of the equation for EXAFS modeling. In the EXAFS model

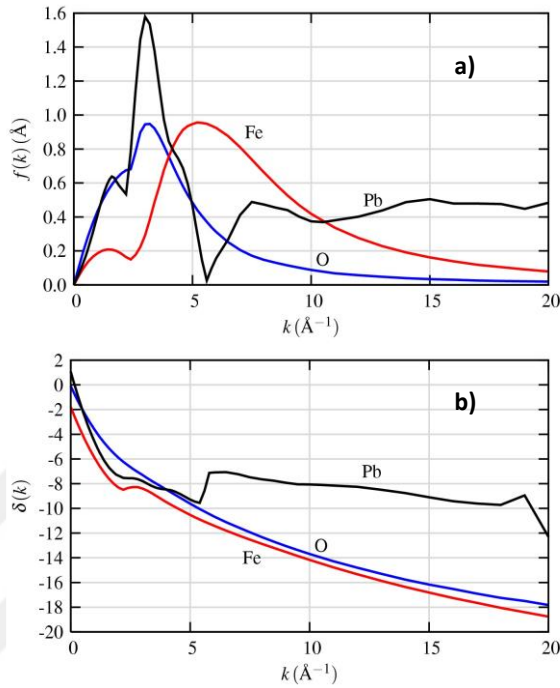
- $f(k)$ , scattering amplitude
- $\delta(k)$ , phase shift and
- $\lambda(k)$ , mean free path of the photoelectron

can be calculated by an ab initio software code for EXAFS called “*FEFF*” which is embedded in the Demeter software package [181]). FEFF calculations use the atomic coordinates, angles, and unit cell parameters to determine the three particular parameters given above for EXAFS modeling. On the other hand, other parameters such as:

- $N$  (coordination number of the corresponding shell)
- $R$  (distance in between the main absorber and neighbor atom) and
- $\sigma^2$ , mean square displacement of  $R$  as a function of thermal motion

are estimated using the experimental spectroscopic data. Then final model is generated by comparing the experimental data and the model data as a function of guessed parameters that result in the examination of local structure of the main absorber. Although, the simple derivation of EXAFS equation is given above, a more detailed discussion and the formal mathematical derivation can be found elsewhere [290], [292], [296].

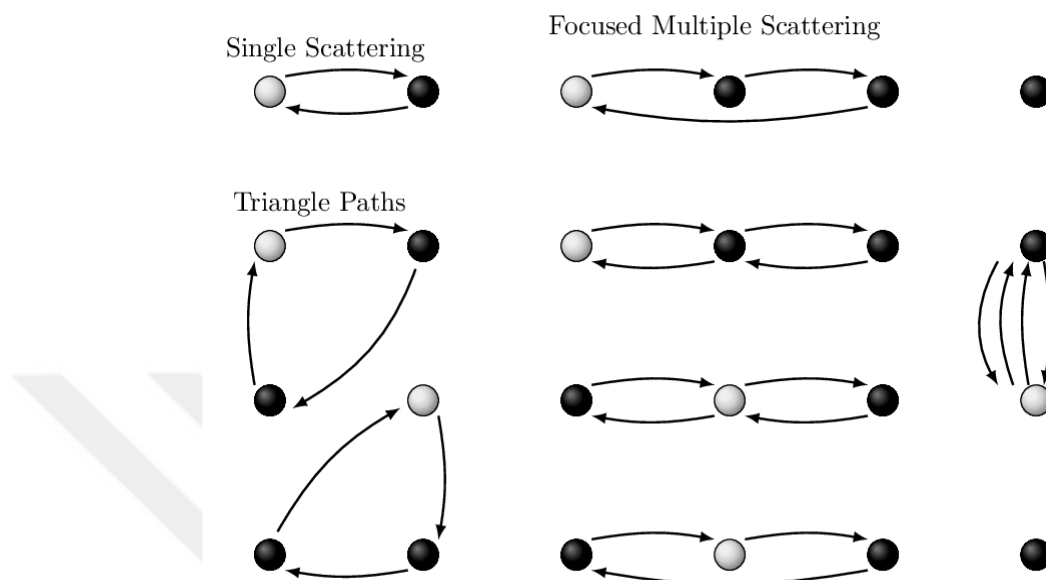
**Influence of the atomic number (Z) effect on  $f(k)$  scattering amplitude and  $\delta(k)$  phase shift:**



**Appendix C16.** Scattering amplitude  $f(k)$  and  $\delta(k)$  phase shift of Fe, Pb and O atoms [292]. Copyright (2020) Mineralogical Society of America.

**Appendix C16** illustrates the scattering amplitude  $f(k)$  and phase shift  $\delta(k)$  of Fe, Pb and O atoms as a function of  $k$ .  $f(k)$  tends to maximize for intermediate  $k$  values, and decreases for high  $k$  values. Only very heavy elements (*e.g.*, Pb) show reasonable scattering amplitude ( $f(k)$ ) at high  $k$  values. On the other hand, dramatic differences between the line shapes of  $\delta(k)$  for different elements is only visible for extremely heavy elements (*e.g.*, Pb). It can be concluded that if there are more than one element in the same coordination shell, atomic number difference between different elements should be at least 5 to identify the elements involved in scattering by utilizing the corresponding scattering amplitude curves [293]. For instance, in the currently investigated  $\text{LaMnO}_3$  type simple perovskite systems, La is the main absorber and Mn and O ions are present in the first coordination shell. In this structure, Mn and O can be readily identified due to their significant difference in atomic number. On the other hand, in the case of B-site mixed perovskites in the form of  $\text{LaMn}_x\text{Co}_y\text{O}_3$ , distinguishing Mn and Co atoms in the first coordination shell using scattering amplitude  $f(k)$  and/or phase shift  $\delta(k)$  functions may be challenging due to the small difference in their atomic numbers.

### The multiple scattering effect:



**Appendix C17.** The single and multiple scattering path demonstration. White spheres represent the main absorber and the black spheres indicate the neighbouring atoms [292]. Copyright (2020) Mineralogical Society of America.

In general, single scattering from the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> shells contribute predominantly to the EXAFS model but there are cases where multiple scattering events become effective in which generated photoelectron undergoes scattering processes more than once, before it goes back to the main absorber (see **Appendix C17**). Such possible paths are considered in the FEFF calculations and the combination of these single and multiple scattering paths provide an improved theoretical model for the experimental data. Therefore, it is important to note that all possible scattering paths of the main absorber atom can be utilized in FEFF calculations by providing geometrical parameters of the central and neighbor atoms.

### Instrumentation and Sample Preparation for XAFS Experiments

In this section, important aspects of the XAFS instrumentation and experimental sample preparation will be discussed in detail in an attempt to utilize SR sources efficiently. Several critical parameters should be carefully considered prior to the execution of XAFS experiments for acquiring high-quality XAFS data. Lack of such preliminary considerations may lead to low quality XAFS data or render the data acquisition unfeasible.

### Edge selection and Sample Thickness:

The edge energies of the corresponding elements can be found in various literature sources. The Mucal Periodic Table [297] is one of the commonly used websites tabulating parameters relevant for XAFS experiments such as edge energies, atomic weights, atomic numbers, fluorescent emission energies, and material mass densities *etc.* The edge energy selection should be made by considering edge energies of the background atoms and their absorption coefficients to obtain a reasonable edge step ( $\Delta\mu_0$ ) which should be in the range of  $0.2 > \Delta\mu_0 > 2$ . The edge energy of the main absorber should be chosen within an energy interval, where the edge energy does not overlap with any background atom within -150 eV and +700 eV of the edge energy ( $E_0$ ) to avoid additional perturbations in the EXAFS data due to background atoms. In heterogeneous catalyst systems, such background atoms typically originate from the catalytic support material, secondary active metals, promoters, and catalyst poisons.

For instance, let us consider a heterogeneous catalyst architecture containing only Pt-Ir bimetallic active sites with a 1:1 atom ratio. For these particular atoms of interest, it may not be possible to reach high enough energies to cover the K-edge energies corresponding to Pd and Ir due to the maximum energy limitation of the particular experimental XAFS beamline. In such a case, rather than K-edges, L and M edges can be considered for EXAFS measurements (note that XANES utilizing K-edges could still be possible in such cases, due to the lower energy window required for XANES analysis in contrast to the higher energy window necessary for EXAFS analysis). Considering the data given in **Appendix C18**, it can be realized that  $L_1$  and  $L_3$  edges of Pt may be reasonable for EXAFS analysis, as these regions do not overlap with that of Ir. However, it may not be possible to execute EXAFS measurements for Ir since all of the Ir L and M edges overlap with Pt edges. Additionally, the fraction of Pt or Ir in the first coordination shell cannot be distinguished due to very close atomic numbers of Pt and Ir (*i.e.*, insufficient scattering amplitude and poor phase shift alteration). On the other hand, coordination number and coordination geometry could be still identified.

**Appendix C18. Edge energy values for Pt and Ir [297].**

| Element       |            | Edge Energies (keV) |            | Edge jumps |            | Fluorescence yield |             |
|---------------|------------|---------------------|------------|------------|------------|--------------------|-------------|
| Symbol        | Pt         | K                   |            | K          |            | K                  |             |
| Z             | 78         | L1                  | 13.8920002 | L1         | 1.15978312 | L1                 | 0.114000000 |
| Atomic Weight | 195.089996 | L2                  | 13.2729998 | L2         | 1.40999997 | L2                 | 0.321000010 |
| Density       | 21.3700008 | L3                  | 11.5640001 | L3         | 2.63199997 | L3                 | 0.305999994 |
|               |            | M                   | 3.29699993 |            |            |                    |             |
|               |            | K-alpha             | 66.8199997 |            |            |                    |             |
|               |            | K-beta              | 75.7360001 |            |            |                    |             |
|               |            | L-alpha             | 9.44099998 |            |            |                    |             |
|               |            | L-beta              | 11.0690002 |            |            |                    |             |

| Element       |            | Edge Energies (keV) |            | Edge jumps |            | Fluorescence yield |             |
|---------------|------------|---------------------|------------|------------|------------|--------------------|-------------|
| Symbol        | Ir         | K                   |            | K          |            | K                  |             |
| Z             | 77         | L1                  | 13.4239998 | L1         | 1.15978658 | L1                 | 0.119999997 |
| Atomic Weight | 192.199997 | L2                  | 12.8240004 | L2         | 1.40999997 | L2                 | 0.307999998 |
| Density       | 22.4200001 | L3                  | 11.2150002 | L3         | 2.38700008 | L3                 | 0.294000000 |
|               |            | M                   | 3.17199993 |            |            |                    |             |
|               |            | K-alpha             | 64.8860016 |            |            |                    |             |
|               |            | K-beta              | 73.5490036 |            |            |                    |             |
|               |            | L-alpha             | 9.17300034 |            |            |                    |             |
|               |            | L-beta              | 10.7060003 |            |            |                    |             |

Sample thickness is an important parameter that helps to decide which XAFS experimental mode should be used (*i.e.*, transmission or fluorescence). Absorption length ( $1/\mu$ ) is the most important factor to determine the thickness limit of the sample.

Mucal Periodic Table website [297] provides the absorption lengths at a given energy which can change in accordance with x-ray energy (when we rearrange the equation (A- 2) the correlation between absorption length and energy can be found to be  $1/\mu \approx E^3$ ). Bunker G. [290] states that in order to avoid experimental problems due to sample thickness, as a rule of thumb, total sample thickness including the substrates, should not exceed 4 times of the absorption length. It is important to note that in order to improve the homogeneity of the prepared samples, sample materials are often mixed with X-ray transparent and chemically inert diluents such as BN (Boron Nitride).

We can illustrate how we can address the issues mentioned above with an example. First of all, ABSORBIX (a free-ware located within the Multiplatform Applications for XAFS, MAX software package) written by Alain Michalowicz [298] can be used to calculate the absorption step as a function of sample thickness. The previously discussed example Pt-Ir sample with 1:1 atom ratio can be used to illustrate the thickness effect on XAFS experiments. As mentioned above,  $L_3$  edge of Pt is a reasonable choice in terms of analysis energy interval. However, exact analysis mode (*i.e.*, either fluorescence or as transmission) should also be decided. From the website given above,  $1/\mu$  of Pt at 11564 eV is approximately estimated to be  $2.43 \mu\text{m}$  (micrometers). Thus, the total sample thickness should not exceed  $10 \mu\text{m}$ . In other words, Pt-Ir sample should be crushed to obtain a grain size less than  $10 \mu\text{m}$ .

Pure Sample Absorbance
Quit

### Edge jump optimization for a pure sample without solvent

Ir 1 ☐
Pt 1 ☒

☐ K
☐ LI
☐ LII
☒ LIII
☐ M
Edge  eV

Molar mass  g/mol
Density  g/cm3

Click to fix the Absorbance Jump

☒ Absorbance jump at the edge

$\Delta(\mu X)$

Click to fix the sample weight/cm2

☐ Sample Mass/cm2

g/cm2

Click to fix the thickness

☐ Sample Thickness

cm

$\mu X$  before edge

after edge

The sample mass/surface (g/cm2) is calculated according the typed absorption jump

HELP
Valid

Table Absorbance Calculator
Initialize Sample
Go to Sample
SAVE
Self-Absorption

Pure Sample Absorbance
Quit
Ir 1 ☐
Pt 1 ☒
☐ K
☐ LI
☐ LII
☒ LIII
☐ M
Edge  eV
Molar mass  g/mol
Density  g/cm3

Click to fix the Absorbance Jump

☒ Absorbance jump at the edge

$\Delta(\mu X)$

Click to fix the sample weight/cm2

☐ Sample Mass/cm2

g/cm2

Click to fix the thickness

☐ Sample Thickness

cm

$\mu X$  before edge

after edge

The sample mass/surface (g/cm2) is calculated according the typed absorption jump

HELP
Valid
Table Absorbance Calculator
Initialize Sample
Go to Sample
SAVE
Self-Absorption

**Appendix C19.** The calculation of XAFS sample thickness as a function of edge -step for Pt L<sub>3</sub> edge of Pt-Ir (1:1) sample by using ABSORBIX [298].

**Appendix C19** indicates the amount of material per area and sample thickness in accordance with the corresponding edge-step. These results point out that for an edge-step parameter that is equal to 2 (left panel) yields approximately 34 mg sample with a corresponding thickness of 49  $\mu\text{m}$ . However, this particular thickness exceeds the maximum absorption length and thus is not acceptable. On the other hand, 3.4 mg sample mass corresponding to 4.9  $\mu\text{m}$  sample thickness is reasonable for a 0.2 edge step. Hence, for transmission XAFS experiments, 6.4 mg sample per  $\text{cm}^2$  (BN can be used to dilute the sample to reach a desired mass/area ratio) and 9.8  $\mu\text{m}$  sample thickness could be utilized to use 0.4 edge-step.

Along these lines, in a different Pt-Ir sample with a 1:99 atomic ratio, Pt L<sub>3</sub> edge can be used to avoid edge energy overlaps. **Appendix C20** points out the corresponding amount of sample and sample thickness for 0.2 edge-step ( $\Delta\mu_0$ ). It can be seen that, a sample thickness of 1300  $\mu\text{m}$  is required to provide the desired edge-step, which is much higher than the allowed absorption length. For sample thicknesses above 10  $\mu\text{m}$ , EXAFS oscillations would significantly be attenuated leading to low signal to noise ratio (S/N ratio) due to poor transmission. In such cases, florescence mode experiments can be considered as an alternative option to conduct XAFS studies.

Pure Sample Absorbance

## Edge jump optimization for a pure sample without solvent

 Quit

Ir 0.99 Pt 0.01  
☐ Ir ☒ Pt

☐ K ☐ LI ☐ LII ☒ LIII ☐ M Edge  eV

Molar mass  g/mol Density  g/cm3

Click to fix the Absorbance Jump      Click to fix the sample weight/cm2      Click to fix the thickness

☒ Absorbance jump at the edge      ☐ Sample Mass/cm2      ☐ Sample Thickness

$\Delta(\mu X)$         g/cm2       cm

$\mu X$  before edge  after edge  The sample mass/surface (g/cm2) is calculated according the typed absorption jump

 HELP       Valid

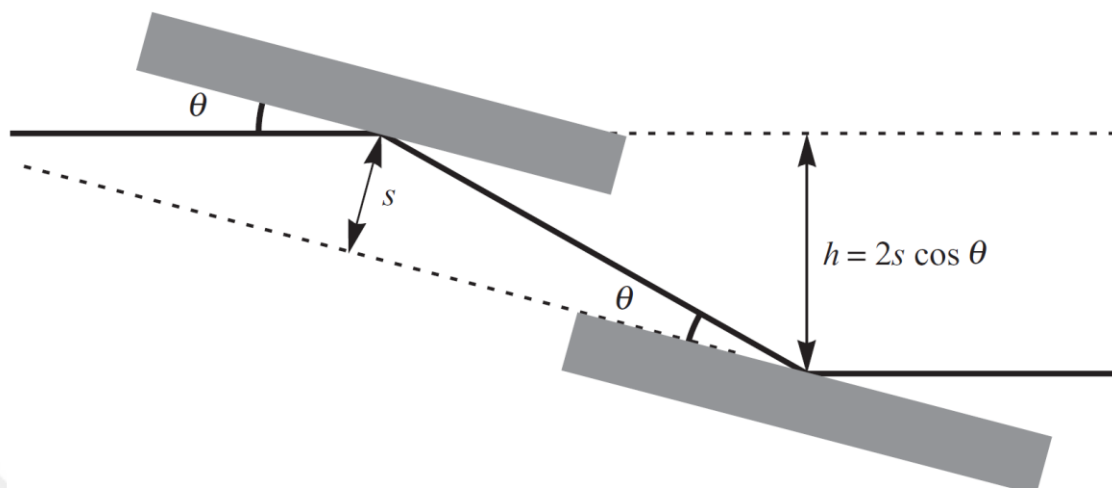
 Table  Absorbance Calculator  Initialize  Sample  Go to Sample  save  Self-Absorption

**Appendix C20.** The calculation of sample thickness as a function of edge-step for Pt  $L_3$  edge of Pt-Ir (1:99) sample by using ABSORBIX [298].

## Basic Instrumentation for XAFS experiments:

### Monochromator:

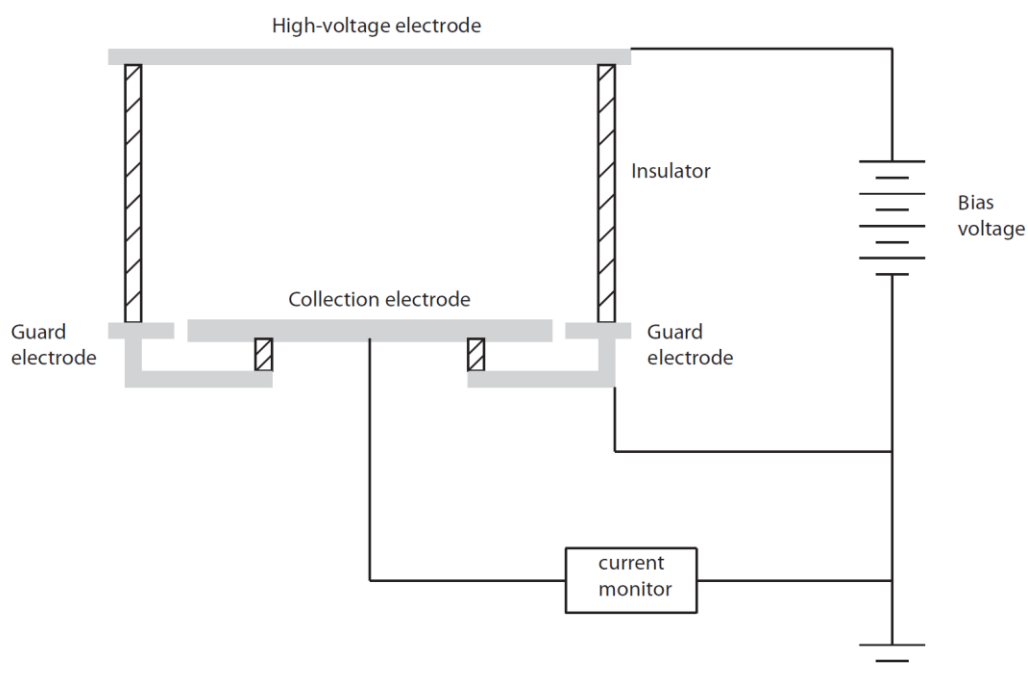
As it was shown in **Appendix C5** and **Appendix C8** after the ID or Bending Magnet, beam energy can be tuned using a monochromator. In general, the SR resolution for X-rays is in the level of hundreds or thousands of eV based on the design of ID or Bending magnets respectively. Typically, XAFS experiments require an energy resolution of ca. 1 eV resolution (*i.e.*, 50% of the core-hole energy width [290]) for incident X-rays which can be obtained by using custom-design x-ray optics. The double crystal monochromator is the most common X-ray optic tool in XAFS instrumentation. The energy of the incoming X-rays is selected by arranging the angle of incidence of the incoming beam on the first crystal (hard X-ray alignment), followed by the second crystal (soft x-ray alignment). The materials of crystals and their diffraction planes are chosen in accordance with the energy interval of the corresponding beamline by considering Bragg's law limitations. For example, Si crystals cannot be used for the energies lower than 2 keV due to inelastic scattering.



**Appendix C21.** The illustration of a double crystal monochromator: left crystal (hard x-ray alignment), right crystal (soft x-ray alignment) [290]. Copyright (2020) Wiley.

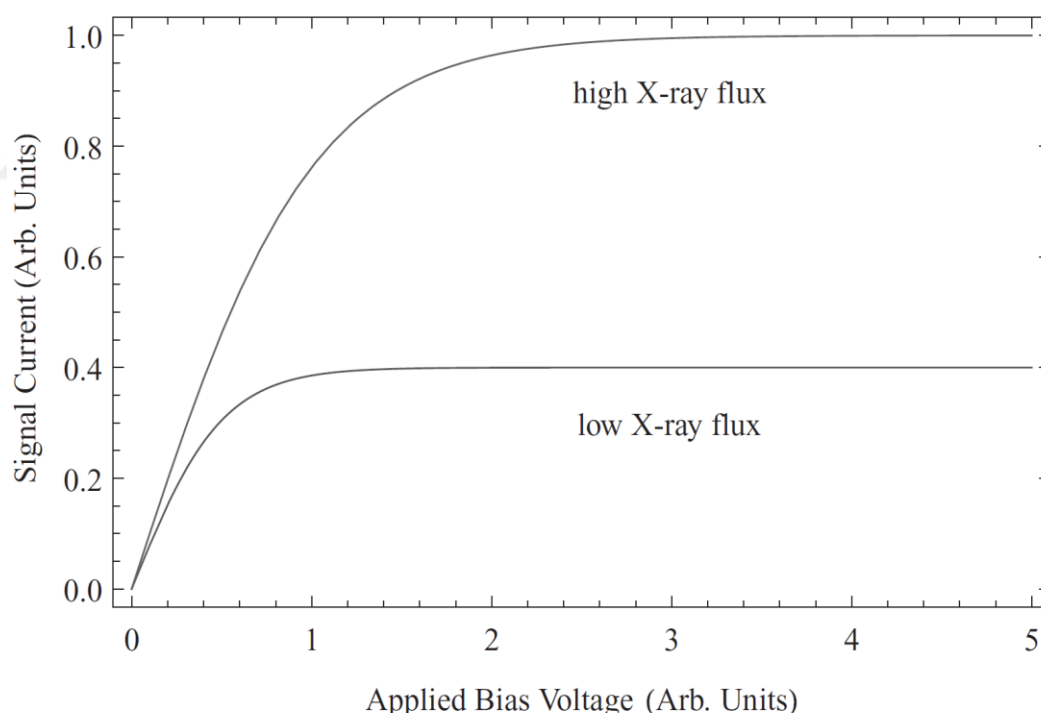
### Ionization Chambers:

Absorption is measured by measuring the intensity difference between the incoming (before the sample) and the outgoing (after the sample) X-ray beam. Ionization detectors are typically used to convert photochemically activated ionized gas molecules to an electrical signal. The ionization chambers consist of a pair of electrodes that are filled with an inert gas.



**Appendix C22.** The ionization detector diagram adapted from [299].

The **Appendix C22** indicates the internal structure of an ionization detector. By applying a few hundred-volt potential in between electrodes, an electric field is generated mobilize the photo ionized gas molecules. Gas molecules present between the electrodes provide a reasonable electrical insulation in the absence of X-rays. Upon ionization, the negatively charged particles are moved towards the anode and positively charged ions are moved towards cathode. This charge separation generates an electric current on the order of  $10^{-7}$ - $10^{-11}$  A, where precise amplifiers are used to measure the current change. The applied electric field should be sufficient to separate electro-cation pairs prior to their recombination. Since there is a possibility of secondary ionization of the gas molecules based on the kinetic energy of electron ion pairs, the bias voltage, which generates electric field, must not be too high (applied electric field can accelerate these particles and lead to secondary ionization).



**Appendix C23.** Current generation as a function of applied bias responsible in an XAFS ionization chamber [290]. Copyright (2020) Wiley.

**Appendix C23** shows increase of the signal current with increasing bias voltage in the ionization chambers and the saturation of the signal at elevated voltages for two different magnitudes of X-ray flux. During the optimization of the ionization detectors, a constant x-ray flux is applied until reaching to the plateau region. Otherwise, X-ray induced

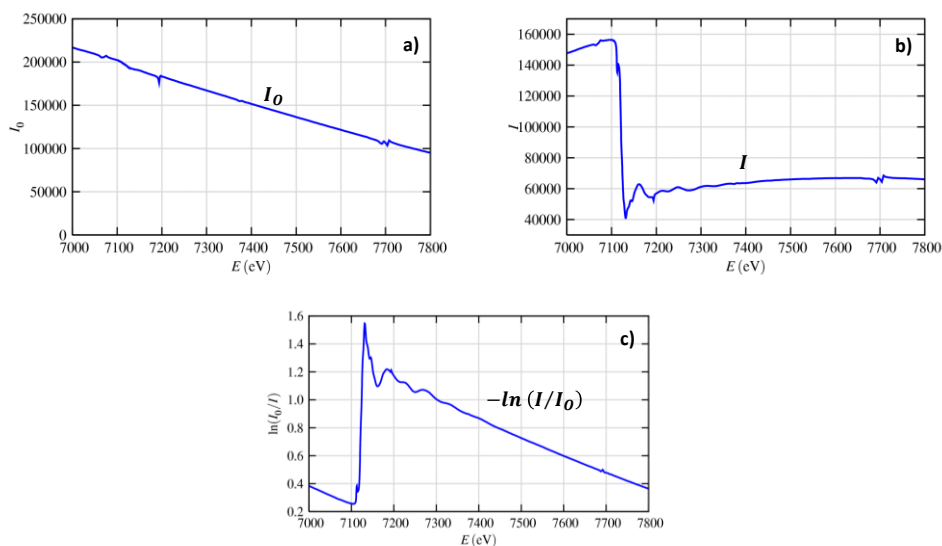
photocurrent may not reflect the exact number of photons due to the low bias or secondary ionization of the gas particles in the ionization detector. An additional requirement for the ionization detectors is to choose a suitable gas mixture based on the energy of incoming x-ray photons. In general, helium, nitrogen and argon are commonly used in ionization detectors. However, based on the energy dependent absorption coefficient of the filling gases, a mixture should be chosen in accordance with edge energy of the sample. The XAFS mass program [300] is able to calculate the mixture of the gases along with the energy requirements.

### Data Analysis for XAFS Experiments

In this section, XAFS data analysis and basics of EXAFS modeling issues will be summarized which can be used to avoid incorrect interpretation of the absorption data.

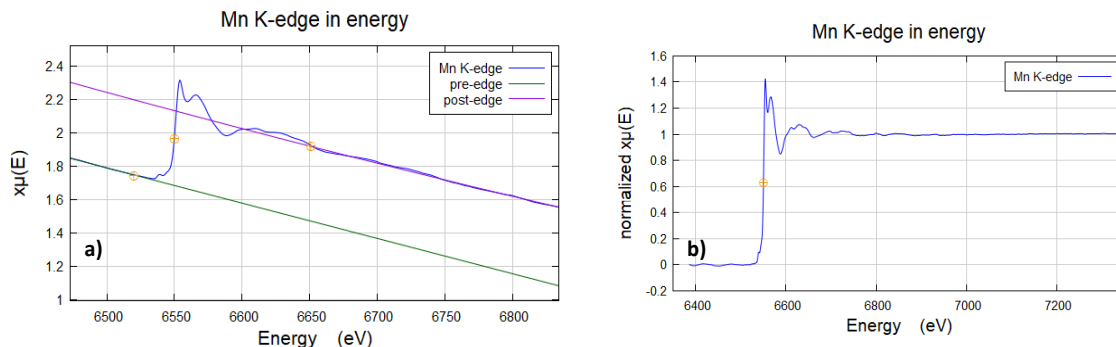
#### XAFS Data Reduction

In general, for the XAFS data analysis Demeter software package (<https://bruceravel.github.io/demeter/>) can be used [181]. Prior to investigate the XANES and/or EXAFS region, the X-ray intensity data should be converted to the absorption coefficient data where equation (A- 1) can be used to calculate  $\mu(E)$  for transmission mode experiments. **Appendix C24** illustrates the construction of the  $\mu(E)$  curve using the incoming ( $I_0$ ) and outgoing ( $I$ ) beam intensities.



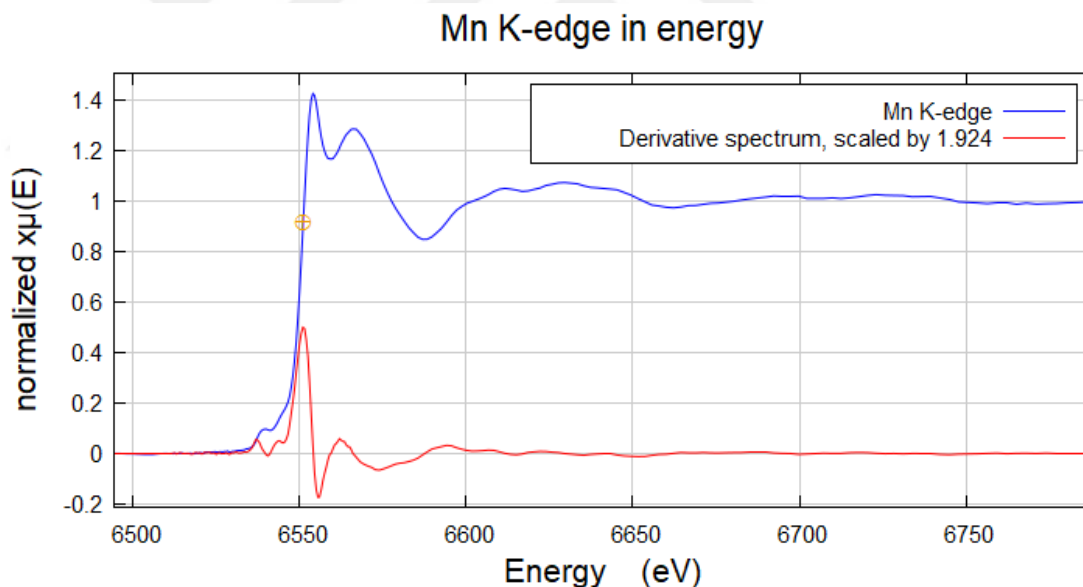
**Appendix C24.** The conversion of XAFS signals to  $\mu(E)$  for Fe K-edge in FeO where a)  $I_0$ , b)  $I$ , and c)  $\ln(I/I_0)/\mu(E)$  [292]. Copyright (2020) Mineralogical Society of America.

Next, pre-edge and post-edge alignment is accomplished followed by normalizing of the data. As a result,  $\mu(E)$  is set to 0 and the post edge  $\Delta\mu_0$  is set to 1.



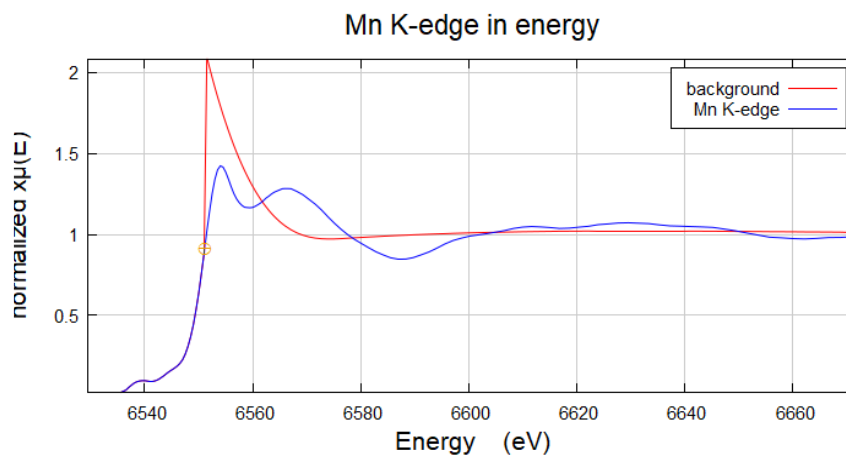
**Appendix C25.** The Mn K-edge XAFS data a) before normalization, and b) after normalization.

The Mn x-ray absorption data given in **Appendix C25a** is processed using Athena software [181], where pre-edge and post edge polynomial normalization functions are applied to the raw data to obtain **Appendix C25b**.



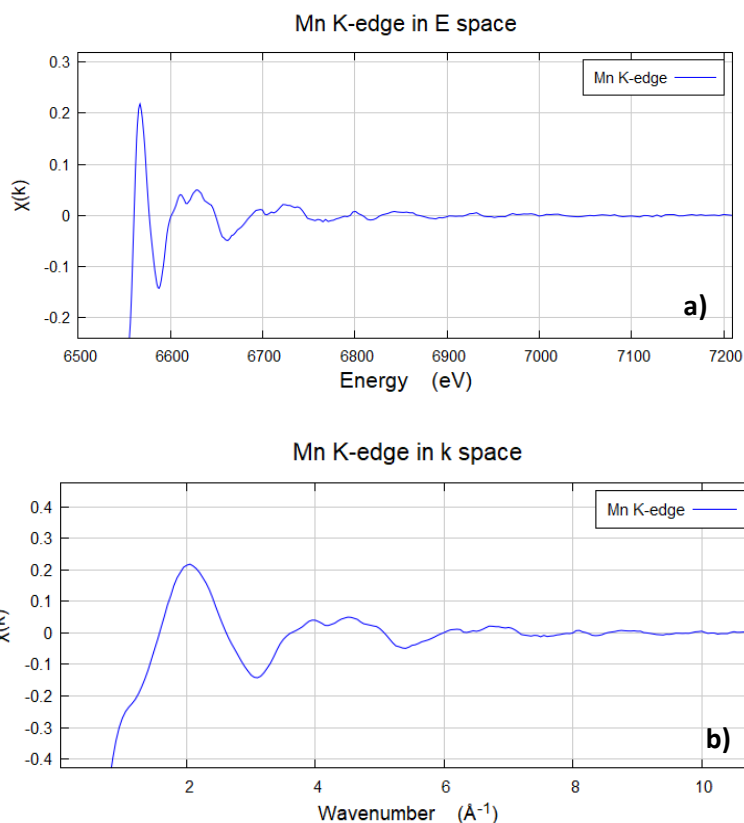
**Appendix C 26.** Absorption data and its 1<sup>st</sup> derivative for Mn K-edge.

The  $E_0$  (edge-energy) can be determined by taking the 1<sup>st</sup> derivative of the absorption data as shown in **Appendix C26**. The position and energy shift of  $E_0$  is especially important for XANES interpretation.



**Appendix C27.** The absorption data of Mn K-edge and the background function.

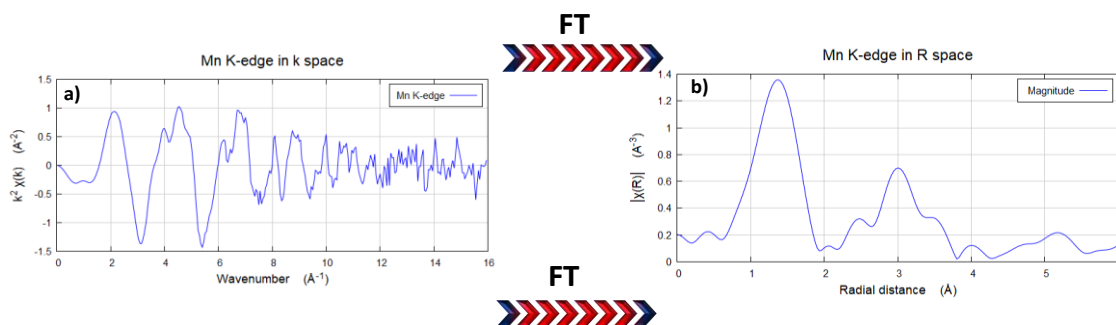
In the XAFS theory section, background function is already mentioned. Hence, the background function can be considered as the absorption coefficient without scattering and it is subtracted from the absorption data to isolate the EXAFS oscillations (**Appendix C27**). The background subtracted versions of the EXAFS data in energy and  $k$  space are shown in **Appendix C28**.



**Appendix C28.** The background subtracted Mn K-edge data in a) E space and b) k space.

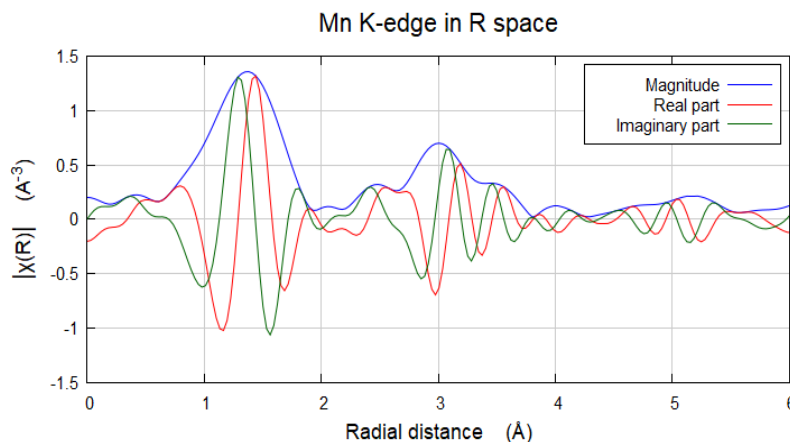
## EXAFS Data Analysis

To analyze the EXAFS region scattering oscillations, the data must be transformed to a sinusoidal function. To achieve this, oscillations should be converted from E-space to  $k$ -space and weighted with  $k^2$  to prevent the attenuation of the oscillations at high E or  $k$  (see **Appendix C28** and **Appendix C11**, respectively). Finally, the Fourier Transform (FT) of  $\chi(k)$  transforms  $k$ -space to R-space (radial distribution).



**Appendix C29.** The FT of a)  $k^2 \chi(k)$  to b)  $\chi(R)$  in R-space for Mn K-edge.

The transformation of  $k^2 \chi(k)$  to  $\chi(R)$  is indicated in **Appendix C29**.  $\chi(R)$  is a complex function. Therefore,  $\chi(R)$  contains both real,  $\text{Re}[\chi(R)]$  and imaginary,  $\text{Im}[\chi(R)]$  components which should be used in the EXAFS modeling.

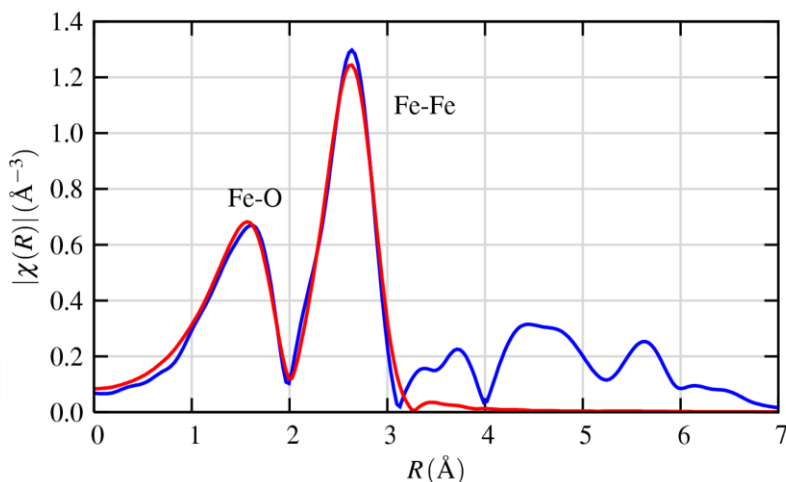


**Appendix C30.** The illustration of  $\text{Re}[\chi(R)]$  and  $\text{Im}[\chi(R)]$  parts of  $\chi(R)$  for Mn K-edge.

There are multiple peaks in **Appendix C30b** which can be assigned to different coordination shells. In this particular case, since the sample is  $\text{LaMnO}_3$ , the first shell most probably consists of O atoms and the second highest contributor could be La atoms.

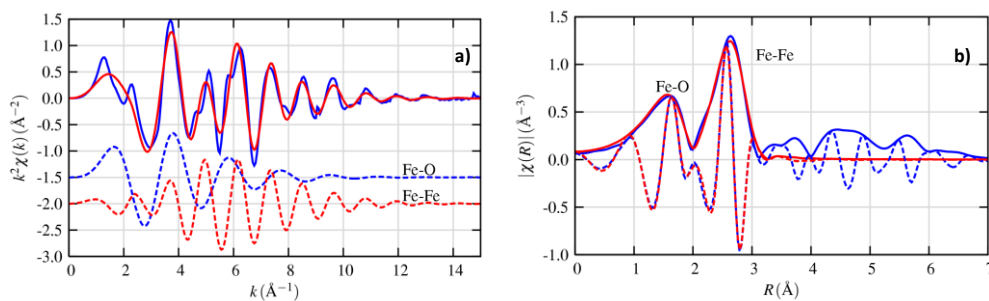
Although, 1<sup>st</sup>, 2<sup>nd</sup> and further shell fitting is typically a multi-step process, in the case of the FeO example (**Appendix C31**), it can be accomplished in a single step. In the EXAFS

modeling, it is important to make an educated guess for the geometric structure of the main absorber based on the preliminary data that can be extracted from benchtop spectroscopic techniques (XRD, TEM *etc.*).



**Appendix C31.** The EXAFS model for FeO where red line is the best fit for the first two shells and blue is the experimental data [292]. Copyright (2020) Mineralogical Society of America.

As depicted in **Appendix C32**, EXAFS modeling consists of the adaptation of FT of sine waves using the proposed model generated by FEFF calculations and implemented by ARTEMIS code in the Demeter software package [181]. Along these lines, scattering amplitude ( $f(k)$ ), phase shift ( $\delta(k)$ ), N (coordination number of the corresponding shell), R (distance between the main absorber and neighbor atom), and mean square displacement ( $\sigma^2$ ) of R as a function of thermal motion are estimated and compared with the experimental data to identify the local chemical environment of the main absorber.



**Fit Results: Uncertainties are in parentheses**

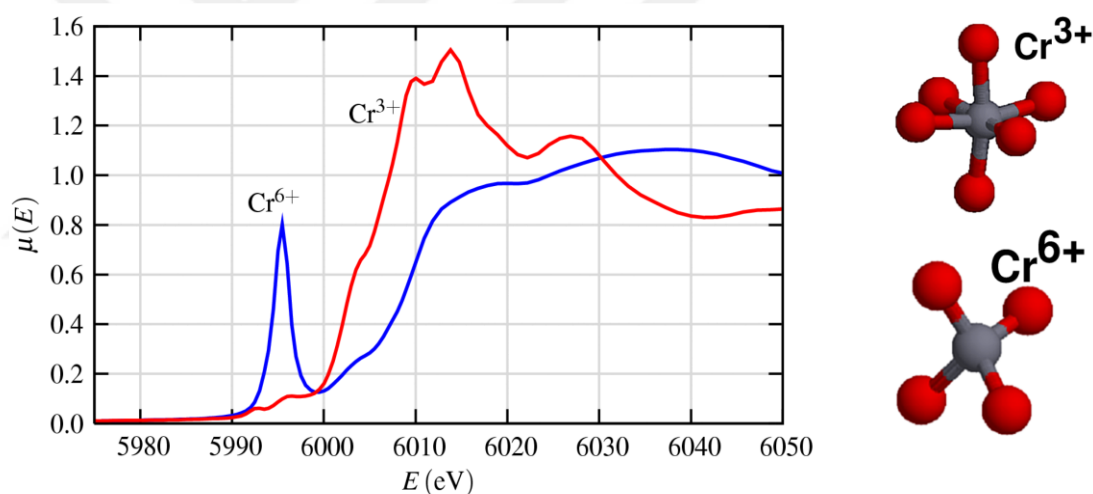
| Shell | N         | R (Å)     | $\sigma^2$ (Å <sup>2</sup> ) | $\Delta E_0$ (eV) |
|-------|-----------|-----------|------------------------------|-------------------|
| Fe-O  | 6.0(1.0)  | 2.10(.02) | 0.015(.003)                  | -2.1(0.8)         |
| Fe-Fe | 11.7(1.3) | 3.05(.02) | 0.014(.002)                  | -2.1(0.8)         |

**Appendix C32.** The EXAFS model and experimental data comparison: a)  $k^2\chi(k)$ , b)  $\chi(R)$  and  $\text{Re}[\chi(R)]$  part of  $\chi(R)$  with fitting results where  $\Delta E_0$  indicates the difference between experimental and theoretical  $E_0$  [292]. Copyright (2020) Mineralogical Society of America.

It is important to remind that in the  $\chi(R)$  curve in **Appendix C32**, the peaks indicate path lengths and there is almost 0.5 Å typical shift in between bond distances and path lengths due to the phase shift in the sine wave ( $\sin [2kR + \delta(k)]$ ) [292].

### XANES Interpretation

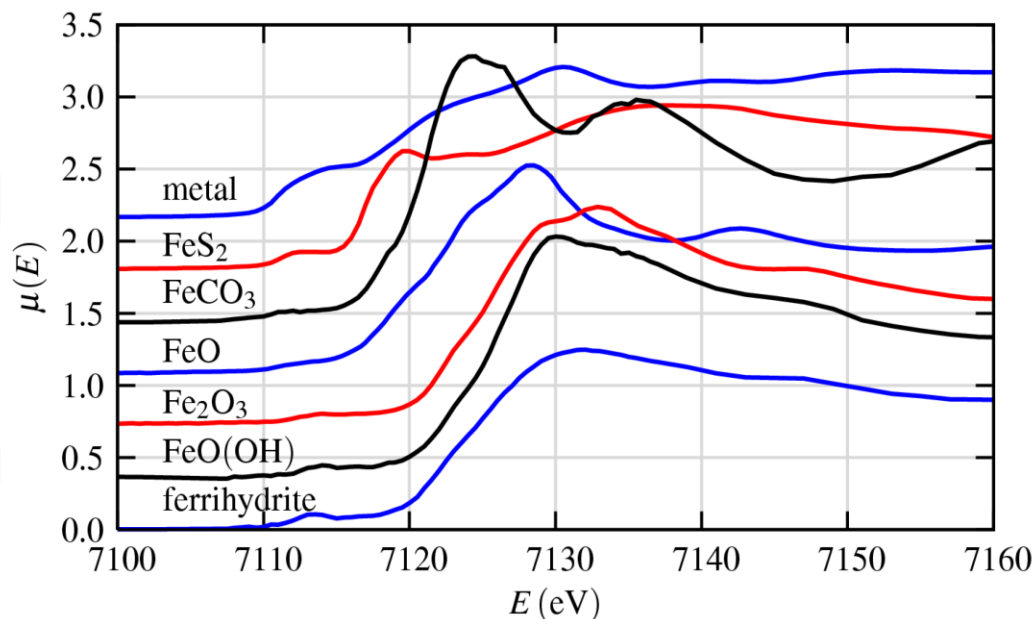
XANES technique is extremely sensitive to coordination chemistry and valence state of the main absorber. The absorption amplitude at the edge is much higher than EXAFS oscillations thus, even for much lower S/N as compared to EXAFS region, near edge data could be utilized to obtain XANES analysis of the main absorber.



**Appendix C33.** XANES data for  $\text{Cr}^{6+}$  (blue) and  $\text{Cr}^{3+}$  (red) [292]. Copyright (2020) Mineralogical Society of America.

In the XANES region, the edge energy typically increases as the formal oxidation state of an atom increases (albeit, exceptions exist, *e.g.*, Au). XANES data presented in **Appendix C33** demonstrates the influence of the coordination chemistry and oxidation state on the edge energy. As seen in **Appendix C33**,  $\text{Cr}^{3+}$  has a lower edge energy than  $\text{Cr}^{6+}$ . Furthermore, in the case of the distorted tetrahedral  $\text{Cr}^{6+}$  system, there is a characteristic sharp pre-edge fingerprint. Partially filled d orbitals can hybridize with p orbitals and this effect increases with the increasing deviation from the ideal octahedral structure towards a distorted tetrahedral structure. As a result, symmetry-forbidden s to d electronic transitions could be allowed which give rise to the occurrence of a sharp pre-edge absorption feature.

Comparison of the edge energy shifts of various samples with a reference sample can be useful to determine the formal oxidation state of the main absorber. By using a linear combination of the XANES spectra of known samples (*e.g.*, XANES spectra of a particular atom with different oxidation states/chemical environments, see **Appendix C34**), XANES spectra of an unknown sample can be estimated. This can be particularly beneficial for samples containing non-uniform structures/compositions or mixtures.



**Appendix C34.** XANES data for a different of Fe species with varying oxidation states [292]. Copyright (2020) Mineralogical Society of America.

## Appendix D

### List of Publications of Kerem E. Ercan

1. Y. Sahin, A. T. Sika-Nartey, K. E. Ercan, Y. Koçak, S. Şenol, E. Ozensoy, Y. E. Türkmen “Precious Metal-Free  $\text{LaMnO}_3$  Perovskite Catalyst with an Optimized Nanostructure for Aerobic C-H Bond Activation Reactions: Alkylarene Oxidation and Naphthol Dimerization,” *ACS Applied Materials & Interfaces*, 2021 (13) 5099-5110.
2. M. Kurt, Z. Say, K. E. Ercan, E. I. Vovk, C. H. Kim, and E. Ozensoy, “Sulfur Poisoning and Regeneration Behavior of Perovskite-Based NO Oxidation Catalysts,” *Topics in Catalysis*, vol. 60, no. 1, pp. 40–51, Feb. 2017.
3. S. Bac, Z. Say, Y. Kocak, K. E. Ercan, M. Harfouche, E. Ozensoy, A. K. Avci, “Exceptionally active and stable catalysts for  $\text{CO}_2$  reforming of glycerol to syngas,” *Applied Catalysis B Environmental*, vol. 256, p. 117808, Nov. 2019. **(First Scientific Paper of SESAME, Jordan).**
4. Z. Say, O. Mihai, M. Tohumeken, K. E. Ercan, L. Olsson, and E. Ozensoy, “Sulfur-tolerant  $\text{BaO/ZrO}_2/\text{TiO}_2/\text{Al}_2\text{O}_3$  quaternary mixed oxides for  $\text{deNO}_x$  catalysis,” *Catalysis Science and Technology*, vol. 7, no. 1, pp. 133–144, 2017.
5. S. Polat Genlik, D. Tigan, Y. Kocak, K. E. Ercan, M. O. Cicek, S. Tunca, S. Koylan, S. Coskun, E. Ozensoy, E. Unalan, “All-Solution-Processed, Oxidation-Resistant Copper Nanowire Networks for Optoelectronic Applications with Year-Long Stability,” *ACS Applied Materials & Interfaces*, vol. 12, no. 40, pp. 45136–45144, Sep. 2020
6. M. Çağlayan, M. Irfan, K. E. Ercan, Y. Kocak, and E. Ozensoy, “Enhancement of Photocatalytic  $\text{NO}_x$  Abatement on Titania via Additional Metal Oxide  $\text{NO}_x$ -Storage Domains: Interplay Between Surface Acidity, Specific Surface Area, and Humidity,” *Applied Catalysis B Environment*, p. 118227, Sep. 2019.

7. M. Kurt, Z. Kap, S. Senol, K. E. Ercan, A.T. Sika-Nartey, Y. Kocak, A. Koc, H. Esiyok, B. S. Caglayan, A. E. Aksoylu and E. Ozensoy “Influence of La and Si Promoters on the Anaerobic Heterogeneous Catalytic Decomposition of Ammonium Dinitramide (ADN) via Alumina Supported Iridium Active Sites” *Applied Catalysis A* (Submitted)
8. K. E. Ercan, Z. Say, M. Kurt, M. Karatok, A. T. Sika-Nartey, E. Ozensoy, “Remarkable CO/NO Oxidation Performance of Precious Metal-Free Perovskites at Severe Reaction Conditions.” *Journal of Physical Chemistry C* (Submitted).
9. Z. Say, M. Kaya, Ç. Kaderoğlu, Y. Koçak, K. E. Ercan, A. T. Sika-Nartey, C. Langhammer, E. Ozensoy, “High Resolution Chemical Identification of Catalytic Poisoning Species on Metal/Metal Oxide Interfaces with Near-field Nano-Infrared Spectroscopy.” *Journal of American Chemical Society* (Submitted).
10. M. Ozden, Z. Say, Y. Koçak, K. E. Ercan, E. Ozensoy, A. K. Avcı “Syngas Production by CO<sub>2</sub> Reforming of Glycerol on Ru-Based Catalysts: Unraveling the Interplay Structure and Reactivity.” *Applied Catalysis A* (Accepted in Press).
11. K. E. Ercan, Z. Kap, A. T. Sika-Nartey, Y. Koçak, Z. Say, E. Ozensoy “Catalytic Performance Exploration of Fe/CeO<sub>2</sub>, Co/Ce/CeO<sub>2</sub> and Fe-Co/CeO<sub>2</sub> Based NO reduction Systems with *In-Situ/Ex-Situ* Spectroscopic Insights.” (in preparation).
12. M. U. Khan, Y. Kocak, Bartu K., A. T. Sika-Nartey, K. E. Ercan, M. Zahmakıran, and E. Ozensoy “Pt Nanoparticle Decorated Two-Dimensional Hexagonal  $\beta$ -Ni(OH)<sub>2</sub> Nanoplatelets Reveal Superior Catalytic Hydrogen Production from N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>.” (In preparation).
13. A. T. Sika-Nartey, Y. Sahin, K. E. Ercan, Z. Kap, Y. Kocak, A. D. Erdali, Y. E. Türkmen and E. Ozensoy “Low-Temperature Aerobic C–H Bond Activation in Alkylarene and Alcohol Partial Oxidation via 2-D Layered Double Metal Hydroxide Nanostructures.” (In preparation).