

**Pt-FREE PEROVSKITE BASED OXIDATION CATALYSTS FOR
AUTOMOTIVE APPLICATIONS**

A THESIS

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE

OF BİLKENT UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

By

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July, 2013

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ABSTRACT

Pt-FREE PEROVSKITE BASED OXIDATION CATALYSTS FOR AUTOMOTIVE APPLICATIONS

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July, 2013

Textural properties, structural integrity and NO_x/SO_x adsorption/release properties of LaMnO₃, Pd/LaMnO₃, LaCoO₃ and Pd/LaCoO₃ type perovskites were studied via in-situ FTIR, ex-situ FTIR, TPD, XRD, XPS and N₂ sorption. Adsorption geometries of NO_x species on the synthesized samples were determined via in-situ FTIR, which revealed similar NO_x adsorption types for all perovskites. The NO_x adsorption capacity (NSC) of LaMnO₃ is higher than that of LaCoO₃, due to the higher specific surface area and the higher crystallization temperature of the Mn-based perovskite. In situ FTIR and TPD experiments showed that incorporation of Pd into the perovskite structure does neither have a significant influence on the type of adsorbed NO_x species nor on the NSC. However, the surface structures of perovskites significantly change after reduction in H₂ atmosphere, leading to drastic increase in the uptake of NO_x. Although NO_x adsorption behavior of LaCoO₃ and Pd/LaCoO₃ are quite similar, Pd has significant influence on preserving the structural integrity of Pd/LaCoO₃ upon reduction with H₂ at 623 K. Moreover, TPD measurements showed that complete reduction of surface nitrite/nitrate groups was observed for Co-based perovskites with the appearance of a N₂ (28 a.m.u) signal. SO_x adsorption/desorption behavior of LaMnO₃, Pd/LaMnO₃, LaCoO₃, and Pd/LaCoO₃, was also investigated via in-situ FTIR. Sulfation of the perovskite surfaces reveals the presence of surface sulfite/sulfate and bulk-like sulfate species. Pd incorporation into both LaMnO₃ and LaCoO₃ significantly increases the SO_x storage on the surface. Investigation of the SO_x release characteristics of LaMnO₃ and Pd/LaMnO₃ showed that although Pd-containing sample stores significantly more SO_x, it can also release a large fraction of the adsorbed SO_x species in a reversible fashion via thermal regeneration. However, this is not the case for Co-based materials. Sulfur poisoning is irreversible

on both LaCoO_3 and Pd/LaCoO_3 with the formation of bulk sulfates where thermal regeneration is not effective. For investigating the reduction of sulfate/sulfite species and the regeneration of the sulfur-poisoned catalysts under reducing conditions, desulfation experiments were performed by utilizing H_2 . This set of experiments showed that although Pd-containing perovskites store more sulfur compared to Pd-free counterparts, they can be efficiently regenerated with H_2 at significantly lower temperatures. Thus, these results suggest that Pd-promoted Mn-based perovskite systems are promising oxidation catalysts revealing high NO_x oxidation capability, high NSC and enhanced sulfur tolerance.

Keywords: Perovskite, NO_x storage, LaMnO_3 , Pd/LaMnO_3 , LaCoO_3 , Pd/LaCoO_3 , SO_x poisoning

ÖZET

OTOMOTİV UYGULAMALARI İÇİN PLATİN İÇERMEYEN PEROVSKİT TABANLI OKSİDASYON KATALİZÖRLERİ

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LaMnO₃, Pd/LaMnO₃, LaCoO₃ and Pd/LaCoO₃ tipi perovskitlerin yapısal özellikleri ve NO_x/SO_x adsorpsiyon / desorpsiyon özellikleri, in-situ FTIR, TPD, XRD, XPS ve BET ile çalışılmıştır. Perovskit üzerindeki NO_x adsorpsiyon geometrileri in-situ FTIR ile belirlenmiştir ve tüm perovskitler benzer NO_x adsorpsiyon profili göstermektedir. LaMnO₃ 'ün NO_x depolama kapasitesi, LaCoO₃ 'den daha fazladır. Bunun nedeni, Mn içeren perovskitin XRD de gösterildiği gibi, daha yüksek sıcaklıklarda kristalleşmesinden dolayı; spesifik yüzey alanının Co içeren perovskite göre daha yüksek olmasıdır. In-situ FTIR ve TPD deneylerinde elde edilen sonuçlara göre, perovskit yapılarına Pd eklenmesi, adsorplanmış NO_x türlerinde veya NO_x depolama kapasitesinde önemli bir değişikliğe yol açmamıştır. Fakat, perovskitler, H₂ (g) ortamında indirgendiklerinde, yüzey yapılarında ciddi değişimler ortaya çıkmaktadır. Bunun sonucu olarak, NO_x depolama kapasitelerinde, ciddi bir artış gözlenmektedir. LaCoO₃ ve Pd/LaCoO₃ malzemelerinin, NO_x adsorpsiyonları ciddi benzerlik göstermesine rağmen, indirgenme ortamında Pd'un perovskit ile birlikte bulunması yapıyı korumada ciddi önem taşımaktadır. Ayrıca, Co içeren perovskitleri üzerinde yapılan TPD deneylerinde, H₂ (g) ile nitrit/nitrat türlerinin tam indirgenmesi sonucu, N₂ (28 a.m.u) sinyali gözlenmiştir. LaMnO₃, Pd/LaMnO₃, LaCoO₃ ve Pd/LaCoO₃ tipi perovskitlerin, SO_x adsorpsiyon ve desorpsiyon davranışları da in-situ FTIR ile incelenmiştir. Perovskitlerin kükürt ile zehrlenmesinden sonra, yüzeyde sülfid/sülfat ve iyonik sülfatlar görülmüştür. Hem Co içeren, hem de Mn içeren perovskitlere Pd eklenmesi sonucunda, SO_x depolamada ciddi artış gözlenmektedir. Pd içeren Mn tabanlı perovskit, Pd içermeyen perovskite göre çok daha ciddi miktarda fazla kükürt depolamasına rağmen; Pd içeren perovskitte depolanan kükürtün büyük kısmı, yüksek sıcaklıkla gerçekleştirilen, ısıl rejenerasyon işlemi

sonucunda, yüzeyden temizlenebilmektedir. Co içeren perovskit için bu geçerli değildir. Kükürt zehirlenmesinin, LaCoO_3 ve Pd/LaCoO_3 perovskitleri için ısıtılarak tersinir olmadığı gözlenmiştir. Sülfat/sülfid türlerinin indirgenmesi ve zehirlenen katalizörlerin rejenerasyonu için perovskitler, H_2 gazı ortamında ısıtılmıştır. Bu deneyler sonucunda, Pd içeren perovskitlerin, Pd içermeyenlere oranla daha çok SO_x tutmasına rağmen, sülfürlerin önemli kısmını düşük sıcaklık ve H_2 ortamında geri bıraktığı görülmüştür. Pd içermeyen perovskitlerde, yüzeydeki SO_x türleri, Pd içerenlere nispeten daha yüksek bir ısıtılabilirliğe ve H_2 (g) ile indirgenmeye karşı daha kuvvetli bir direnç göstermiştir. Ayrıca Co tabanlı perovskitlerin yüzeyindeki SO_x türlerinin, Mn içeren perovskitlere göre daha kararlı olduğu saptanmıştır. Tüm bu sonuçlar toplu olarak değerlendirildiğinde, Mn temelli ve Pd ile katkılandırılmış perovskitlerin, yüksek NO_x oksitleme ve depolama potansiyeline ve yüksek kükürt direncine sahip umut verici bir oksidasyon katalizörü olduğu sonucuna varılmıştır.

Anahtar Kelimeler: Perovskit, NO_x depolama, LaMnO_3 , Pd/LaMnO_3 , LaCoO_3 , Pd/LaCoO_3 , SO_x zehirlenmesi

Dedicated to My Family

ACKNOWLEDGEMENTS

Herewith this acknowledgement, I would like to state my gratitude to many individuals who have provided me great support and helped me throughout my studies for my research project.

First and foremost, I would like to express my deep sense of appreciation to my research supervisor Assist. Prof. Emrah Özensoy for providing me an opportunity to work on this research project. I would like to state my sincere thanks to him for his valuable guidance, encouragement, patience and supervision throughout my studies. It has been a pleasure studying in his research group.

I would like to thank especially to Zafer Say for his advice on my research and the precious time that he has shared with me through my graduate studies.

I am sincerely grateful to Evgeny Vovk for his contributions and scientific discussions.

I would like to gratefully thank to General Motors Company for their financial support.

I have received great support, encouragement and companionship from Özlem Ünal, Gözde Barım, Yiğit Altay, Tuğçe Durgut and Menekşe Koca in both my personal life and academic study during the past few years. I thank them all for their valuable friendship.

Last but not the least, I wish to thank to my beloved parents; my mother, Banu Doğaç, my father, Ali Doğaç, my sister, Melis Doğaç and my lovely dog, Roko. Nobody has been more important to me in the world than my family. There is no word to express my gratitude to my family for their love, support and encouragement during my graduate studies. Their unconditional love and continuous support brings me there. I owe them a lot for supporting me spiritually and genuinely throughout my life.

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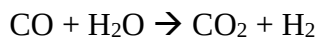
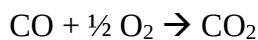
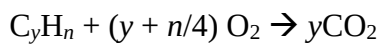
CHAPTER 1

1. INTRODUCTION

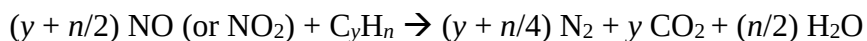
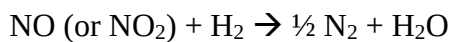
Reducing air pollution caused by toxic gases is an important global problem. In recent years, hazardous gases such as CO, NO_x, SO_x and unburned hydrocarbons have been subject to more stringent emission regulations. NO_x emitted from automobile exhaust have serious effects on the atmosphere, environment and human health [1-3].

To meet emission regulations, the automobile industry is constantly searching for new technologies. The major function of catalytic converters in automotive exhaust systems is performing the following reactions [4];

Oxidation of CO and HC to CO₂ and H₂O:



Reduction of NO (NO₂) to N₂:



Lean burn engines have become very popular in recent years as they offer higher fuel efficiencies and lower CO₂ emission. The major challenge regarding lean burn engines is their high NO_x emissions in the untreated tailpipe. These NO_x gases cannot be removed completely with three way catalysts and emission regulations cannot be met. Thus, various catalyst technologies are considered for NO_x reduction. The catalysts that are used for removing NO_x are selective catalytic reduction (SCR) and NO_x storage and reduction (NSR) catalysts [3]. In SCR catalysts, NO_x are

reduced by H_2 , hydrocarbons (HC) or urea in the presence of excess oxygen. However HC-SCR catalysts suffer from low performance and NH_3 -SCR catalysts have significant technological drawbacks associated with the urea transportation, storage and dosing. NSR technology also has its own set of challenges. The problems with NSR catalysts are sulfur poisoning and the cost of the precious metals (i.e. Platinum Group Metals or PGM) used in their synthesis. Long-term usage of NSR catalysts causes a decrease in the efficiency of the catalysts due to thermal aging and sulfur poisoning. Therefore, the search for novel catalytic technologies for NO_x reduction continues.

Perovskites are widely studied materials in literature and have wide applications in the chemical industry. They are used in oxidation reactions, pollution abatement, hydrogenation and hydrogenolysis reactions, photocatalysis, chemical sensors, and electrolysis, such as solid oxide fuel cells [5-105]. Lanthanum-based perovskite catalysts such as $LaMnO_3$ and $LaCoO_3$ are promising candidates for NSR catalysts due to their higher NO_x conversion, lower price, relatively easy synthesis and higher sulfur tolerance. [5]

CHAPTER 2

2. BACKGROUND

2.1. Properties of Perovskite oxides

2.1.1. Perovskite Structure

The general formula of the perovskite is ABO_3 . Most of the metals that are found in the periodic table are stable in the perovskite structure. The importance of the perovskite structure is that metals can be found in mixed oxidation states and/or unstable oxidation states in the crystal structure. The ideal cubic perovskite structure with a space group $Pm\bar{3}m-O_h$ is shown in Figure 1 [21]. A and B are cations with different sizes, “A” is typically larger than “B”. The “A” position is generally occupied by post-transition metals or alkaline earth metals, and “B” position is generally occupied by transition metals or noble metals. The A and B cations are 12-fold and 6-fold coordinated with oxygen anions, respectively. The perovskite superstructure has a ReO_3 -type framework where the A cation is incorporated into the BO_6 octahedra [21].

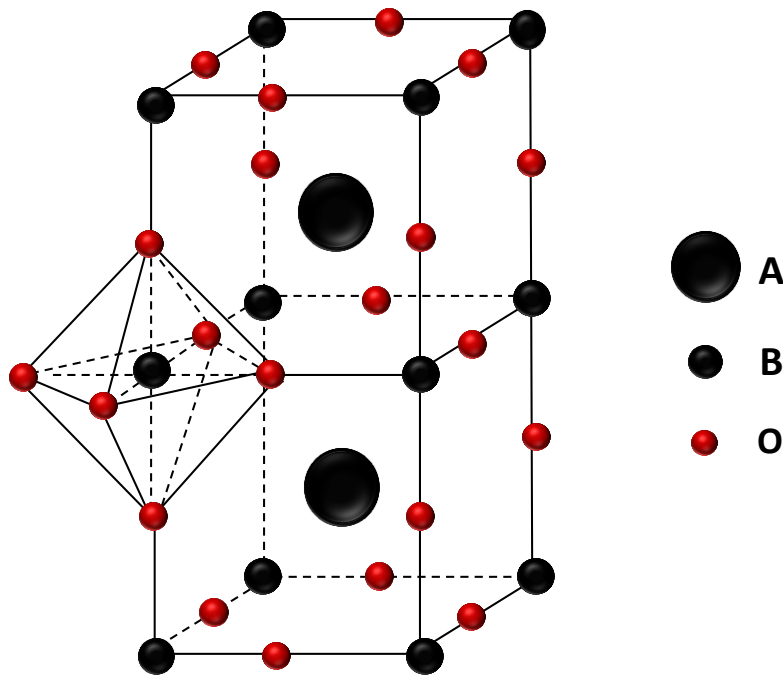


Figure 1. Cubic perovskite crystal structure (adapted from reference 21)

If “a” is considered as a unit cell parameter of ideal perovskite, B-O distance is equal to $a/2$ and A-O distance is $a/\sqrt{2}$. Then, the relationship between the ionic radii becomes

$$r_A + r_O = \sqrt{2} (r_B + r_O)$$

However, cubic structure is still preserved without obeying the previous equation [21]. Goldschmidt [45] introduced a term called the “*tolerance factor*” (t) which is a measure of the deviation from the ideal perovskite crystal structure;

$$t = r_A + r_O / \sqrt{2} (r_B + r_O)$$

where r values are the ionic radii of A and B cations at room temperature [21, 45, 57].

For an ideal perovskite structure, the value of t is equal to 1. This situation is generally observed at high temperatures. Moreover, for values of t between 0.75 and 1, perovskite structure can be still preserved. However, cations of different sizes can alter the structure and lower the symmetry. Rhombohedral, orthorhombic, hexagonal and bixbyite phases are examples of the resulting structures after distortion of the cubic geometry as shown in Figure 2 [3, 46-48].

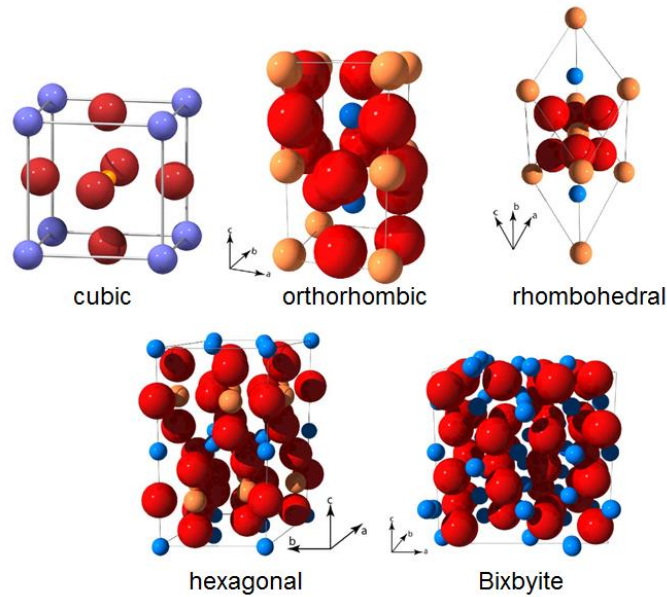


Figure 2. Different crystal structures of perovskite systems [102].

2.1.2. Non-stoichiometry in Perovskites

Non-stoichiometry in the perovskite structure is observed very frequently [21, 49-51]. Other than the ionic radii requirement mentioned above, the electroneutrality condition should also be satisfied. This condition implies that total charge of the A site and B site cations should be equal to the charge of the oxygen anions found in the perovskite structure. Two types of non-stoichiometry are observed for perovskites: oxygen non-stoichiometry and cation non-stoichiometry. For instance, $\text{LaMnO}_{3+\lambda}$ is one of the most commonly known oxygen-rich perovskite structures [52]. However, by substituting different cations into the A and/or B sites, this oxygen non-stoichiometry can be eliminated [53-55]. Another type of non-stoichiometry in perovskites is the cation non-stoichiometry which is common for CaTiO_3 -type perovskites, where some of the Ca cations are missing in the perovskite structure at the A-site position [56]. B-site non-stoichiometry is not as common as previously mentioned cases, because the B-site cations typically possess high charge and small size. Thus, removing these cations from the perovskite structure is thermodynamically unfavorable.

2.1.3. Modification of Perovskite Structure

Moreover, the perovskite structure can be modified by substituting different A and B cations with different cations by keeping the charges and sizes of these latter species comparable with their original counterparts. The A site cation is typically suggested to be catalytically inactive and substitution of different A cations into the structure has two different results; change in the oxidation state of the B site cation and creation oxygen non-stoichiometry [57-59]. Sr^{2+} substitution into the La_2NiO_4 type perovskite is an example of substituting a different A site cation into the perovskite type structure [58]. In this structure, some of the La^{3+} ions are replaced with Sr^{2+} . Since the oxidation states of lanthanum and strontium are different, in order to preserve the electroneutrality, a $\text{Ni}^{2+}/\text{Ni}^{3+}$ couplet is generated and oxygen vacancies are created [58, 59]. Although strontium does not have a direct effect on catalytic performance, the creation of oxygen vacancies and different oxidation states of the Ni cation causes an increase in the oxidation capability of perovskite. Another type of substitution is the insertion of different B site cations into the ABO_3 perovskite structure. B-site substitution is more complicated than A-site substitution because the

B site cation exhibits different oxidation states and it is typically the catalytically active site. However, as in the case of A-site substitution, B-site insertion helps tune the oxidation states of the already existing B-site cations and creates oxygen vacancies which can directly alter the catalytic activity [57, 60-63].

2.1.4. Adsorption Properties of Perovskites

Adsorption properties of perovskites are important for understanding catalytic reaction mechanisms. Tascon et al. studied CO and NO adsorption on LaMO_3 -type perovskite where M is a first-row transition metal; such as Cr, Mn, Fe, Co or Ni [21, 64, 65]. These authors observed that CO adsorption depends on the electronic configuration of the B-site cation at room temperature. The greatest amount of CO is adsorbed on LaFeO_3 , whereas NO adsorption shows maxima for Co and Mn-based perovskites with the formation of dinitrosyls, nitrite and nitrate species on the surface. Kremenec et al. studied the oxygen adsorption of profiles of LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni}$) [66]. Oxygen adsorption profiles are especially important for the reduction/oxidation cycles of the perovskites. Oxygen adsorption is maximized for LaCoO_3 and LaMnO_3 [21, 66, 67].

2.1.5 Thermal Stabilities of Perovskites

Thermal stability of the perovskite structure under reducing conditions is another crucial aspect for the long-term use of catalysts in catalytic cycles. Stability of the catalyst depends on both A and B site cations in the structure [21]. Co-based perovskites are generally very unstable in reducing atmospheres [22, 23, 68-79]. Nakamura et al. showed that partial substitution of Sr into the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ causes important changes in the stability of the perovskite structure [68]. In such cases, stability of the perovskite decreases as the strontium concentration increases. When the Sr concentration increases in the structure, both unstable Co^{4+} cations and oxygen vacancies are formed resulting in the diffusion of bulk oxygen to the surface. Lago et al. examined the reducibility of LnCoO_3 ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$) perovskites [71]. They observed that the Co cations are reduced in two steps: at around 633 K, Co^{3+} is reduced to Co^{2+} and within 783-845 K, Co^{2+} is reduced to metallic cobalt. Moreover, the Ln site of the perovskite determines the stability of the structure and due to the large size of lanthanum, the most stable perovskite in the series is LaCoO_3 . Crespin

et al. have conducted a detailed investigation of the relationship between reduction conditions and the stability of Co-based perovskites [22]. If LaCoO_3 is completely reduced to metallic cobalt and La_2O_3 at 673 K, the reduced phases will return to the original perovskite structure after a re-oxidation process. However, this is not the case when the reduction of LaCoO_3 occurs at 1073 K. Because of the thermal treatment of LaCoO_3 at high temperatures in H_2 atmosphere, metallic Co particles grow drastically in size, so that the original perovskite structure cannot be restored after re-oxidation, and instead Co_3O_4 phase forms. Formation of Co_3O_4 may be prevented via re-oxidation of the reduced phases under very mild conditions.

2.2. Automotive Applications of Perovskites

2.2.1. NO_x Reduction Performances of A and/or B site Substituted La-based Perovskites

Perovskite-type catalysts have been widely applied to exhaust gas treatment systems in the recent years. Kim et al. studied the NO_x reduction performance of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskites [5]. They observed that such catalysts have high inherent NO oxidation capability with or without strontium. However, the effect of strontium addition on NO oxidation is more pronounced for Co-containing perovskites due to a larger amount of oxygen vacancies are created in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. According to their study, although the Co-based perovskite is more active than its Mn-containing counterpart, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is more promising as a commercial catalyst because of the instability of Co-based perovskites in a reducing atmosphere [44, 72]. Li et al. investigated the DeNO_x performance of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ -type perovskites [80]. They used La_2O_3 and SrO as NO_x storage materials. They suggested that the presence of strontium in the perovskite structure is important for two reasons. First, since Sr addition to Co-based perovskites forms an unstable oxidation state of cobalt (i.e., Co^{4+}), the catalyst has a higher oxidation capability. Besides, SrO has a higher basicity than La_2O_3 , so SrO can also act as a NO_x storage component. They found that the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ perovskite had the best NO-to- NO_2 conversion performance and the largest NO_x storage capacity at 300°C. Wen et al. studied NO oxidation via $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ [82]. They observed that the surface is mainly dominated by the A-site cations, i.e. La and Ce. They claimed that there is no direct correlation between catalytic activity and the surface enrichment of A cations.

Among their catalysts, $x=0.2$ has the highest catalytic activity with the highest amount of adsorbed oxygen. Thus, they correlated the catalytic activity with the extent of adsorbed oxygen. On the other hand, this correlation is open to criticism as the perovskite systems which are not doped with Ce but revealing a high oxygen adsorption capacity such as LaCoO_3 , is not as active as the Ce-containing analogue. Hence, extent of adsorbed oxygen should not be the only parameter determining the catalytic activity. NO TPD experiments done by Wen et al. [82] showed that N_2O formation was observed for the Ce-doped perovskite but not for pure LaCoO_3 . The evolution of N_2O might be related to the CeO_2 phase originating from the phase segregation in the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ structure. N_2 signal was not detected for the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ system, excluding the direct decomposition of NO. Removal of NO_x and N_2 production efficiency via a $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ ($0 < x < 0.05$) catalyst was investigated by Zhou et al [84]. This study showed that substitution of cerium increased the stability of the perovskite and the activity of the catalyst, because cerium (IV) was incorporated with the lattice and increased the nickel (II) content that was suggested to be the active site of the perovskite structure. According to their report, $\text{La}_{0.97}\text{Ce}_{0.03}\text{NiO}_3$ had the highest activity during NO conversion. Giannakas et al. [90] studied the reduction of NO over LaMnO_3 and LaFeO_3 -type perovskites. LaMnO_3 and LaFeO_3 showed high activity between 300-500 °C and 300-450 °C, respectively. For LaMnO_3 , $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ pairs were suggested to be responsible for the high activity of the perovskite rather than the specific surface area (SSA). Moreover, the effect of Sr and Ce substitution into LaFeO_3 on the NO+CO reaction was also examined [85]. The catalytic activities of $\text{La}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$, $\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.1}\text{Ce}_{0.1}\text{FeO}_3$ -type perovskites were investigated. Sr-doped perovskites were synthesized successfully whereas Ce could not be incorporated into the perovskite and phase segregation was observed during the synthesis of Ce-doped samples. Activity results showed that the Ce-doped perovskite has the highest conversion of NO+CO whereas the undoped perovskite has the lowest activity [85]. Activities of these perovskite systems were directly correlated to the SSA values. $\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ has the highest activity revealing the highest SSA. Moreover, presence of the CeO_2 phase with the perovskite was found to assist NO combustion [85, 86]. Sr-containing perovskites were deactivated with the formation of SrFeO_3 [85-87]. The effect of Sr doping into LaMnO_3 for NO reduction by CO was examined by Leontiou et al. [92].

These catalysts were found to show activity within 220-560 °C. It was observed that substitution of Sr for La after a certain extent decreased the activity of the catalyst [92] since the Sr addition changes the defects in perovskite structure. It is well known that the LaMnO₃ perovskite has excess oxygen in its lattice [52], however Sr substitution results in an oxygen deficient Mn-based perovskite, leading to a decline in activity.

Lima et al. [88] investigated iron-based perovskites for the following reaction:



Rather than changing the A site of the perovskite, B-site substitution was performed. Co was doped into the B-site of LaFeO₃ rather than Ce and/or Sr that appear at the A site of the perovskite structure. Interestingly, the Co-doped perovskite had a lower activity than undoped LaFeO₃. Another study revealed that when Fe atoms were replaced by Co up to 30%, the activity for NO reduction by CO decreased compared to LaFeO₃ and LaCoO₃ [88, 89]. Co-doped perovskites were also studied by Wang et al [91]. Materials exhibiting different values of x in LaMn_{1-x}Co_xO₃ (where 0 < x < 0.5) were used for NO oxidation. The NO oxidation temperature shifted to lower values with partial substitution of Co into LaMnO₃ in a non-linear fashion. LaMn_{0.9}Co_{0.1}O₃ had the highest activity due to the greatest amount of activated oxygen and the synergistic effect between Mn and Co.

Tanaka et al. [81] analyzed both A-site and B-site substituted perovskites. The catalytic activity and stability of La_{0.9}Ce_{0.1}Co_{1-x}Fe_xO₃ perovskite catalysts (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) for automotive emission control were examined. An increase in the cobalt content increases the catalytic activity and decreases the structural stability. According to their results, Fe was responsible for the structural durability whereas Co improved catalytic activity. Thus, La_{0.9}Ce_{0.1}Co_{0.4}Fe_{0.6}O₃ showed the highest catalytic activity as well as the highest structural durability. It was also reported that when the cobalt fraction exceeds 0.6, the perovskite structure transforms into a K₂NiF₄-type structure that diminishes the activity of the catalyst.

2.2.2. NO_x Reduction Performances of Precious Metal Containing Perovskites

In order to stabilize the precious metal against sintering, volatilization and/or solid state reaction with the substrate, precious metal-containing perovskites are being considered as an important alternative for exhaust treatment systems [21]. Precious metal-containing perovskites were synthesized by either wet-impregnation or co-precipitation methods [5, 83, 94-98]. Kim et al. [5] combined the La_{1-x}Sr_xCoO₃ and La_{1-x}Sr_xMnO₃ perovskites with Pd, in order to increase the efficiency and sulfur poisoning tolerance of the catalyst. It was observed that the Pd/perovskites showed activities as high as commercial catalysts, especially for the conversion of NO to NO₂ [5]. Moreover, the Pd/perovskites were found to be still active after poisoning with sulfur, whereas Pd-free perovskites lost their activity [5]. Rodriguez et al. [83] studied the NO_x performance of LaFe_{0.95-x}Co_xPd_{0.05}O₃-type catalysts. They have shown that by changing the Fe and Co ratio at the B site of the perovskite, NO_x reduction and N₂ selectivity changed. Fe/Co=1 was reported to be the best compositional ratio for NO_x reduction and N₂ selectivity also yielding a catalyst with the highest surface area [83]. They also showed that in the absence of palladium, NO_x conversion decreased drastically. In a different study, NO reduction via H₂ was also investigated on five different perovskites namely, LaFeO₃, La_{0.8}Sr_{0.2}FeO₃, La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O₃, La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ and La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O₃ [93]. Activity results indicated that La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O₃ had the highest conversion at 130 °C whereas the lowest activity was observed for undoped LaFeO₃. All of the substituted perovskites showed similar activity between 210-280 °C. Temperature programmed reduction (TPR) experiments indicated that the extent of reduction of the B-site cations were responsible for the activity towards NO reduction. Moreover, reducibility of the catalysts was enhanced via substitution of Sr and Ce into the perovskites with the creation of oxygen vacancies. The presence of Pd also increased the activity due to its high H₂ chemisorption capability and also due to the ease of perovskite reduction via H spill over. Yao et al. [94] examined the effect of Pd loading on the reduction of NO_x for Co-based perovskites. Catalytic activity was found to be greatly enhanced by the substitution of a slight amount of Pd into the perovskite structure (i.e. LaCo_{0.99}Pd_{0.01}O₃ and LaCo_{0.97}Pd_{0.03}O₃). The increase in the activity of Pd-containing perovskites was associated with the formation of an unusual

oxidation state of palladium, Pd^{4+} [94-97] and a higher SSA compared to Pd-free LaCoO_3 [94, 98].

Tanaka et al. [81] studied palladium supported $\text{La}_{0.9}\text{Ce}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ perovskite catalysts ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) for automotive emission control. They have demonstrated that the activity of the perovskites increased in the presence of Pd. After this study, Tanaka, Uenishi and Nishihata et al. [96, 99-101] introduced a term called “*intelligent catalyst*” for Pd-containing perovskites where it was claimed that the perovskite structure responded to the environmental conditions by maintaining its catalytic performance and structure. Since the catalyst maintained its activity for long periods, it had a “self-regeneration” capability as depicted in Figure 3.

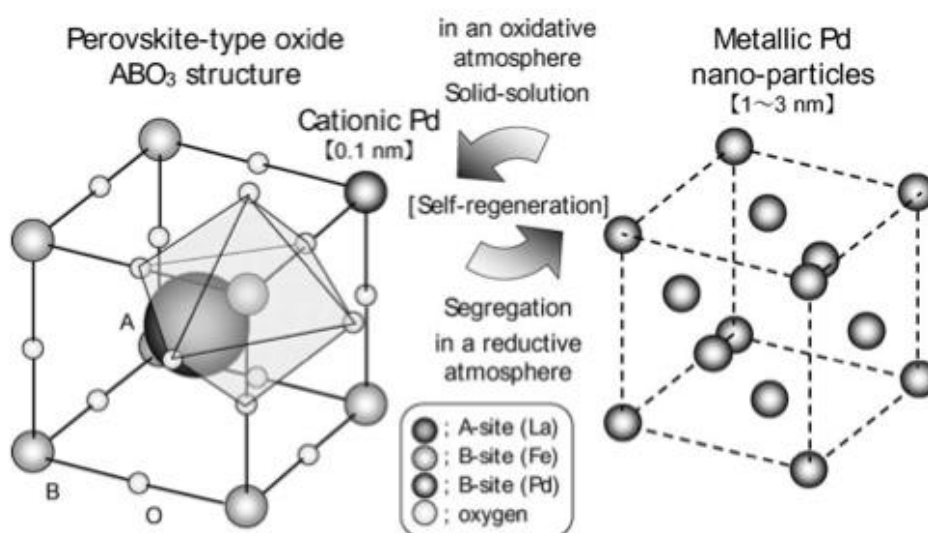


Figure 3. Self-regeneration capability of the Pd containing “*intelligent*” perovskite catalyst [101]

This particular perovskite catalyst was in the form of $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$. According to this report, Pd entered the lattice and occupied the B-site of the perovskite under an oxidizing environment. On the other hand, under a reducing conditions, Pd segregated out of the perovskite lattice and formed a metallic Pd nanoclusters [101]. The presence of the perovskite structure was claimed to inhibit the excessive growth of the metallic Pd particles. Thus, it was suggested that the noble metal-containing perovskite preserved its activity by switching between these two different Pd forms in the catalyst (Figure 4).

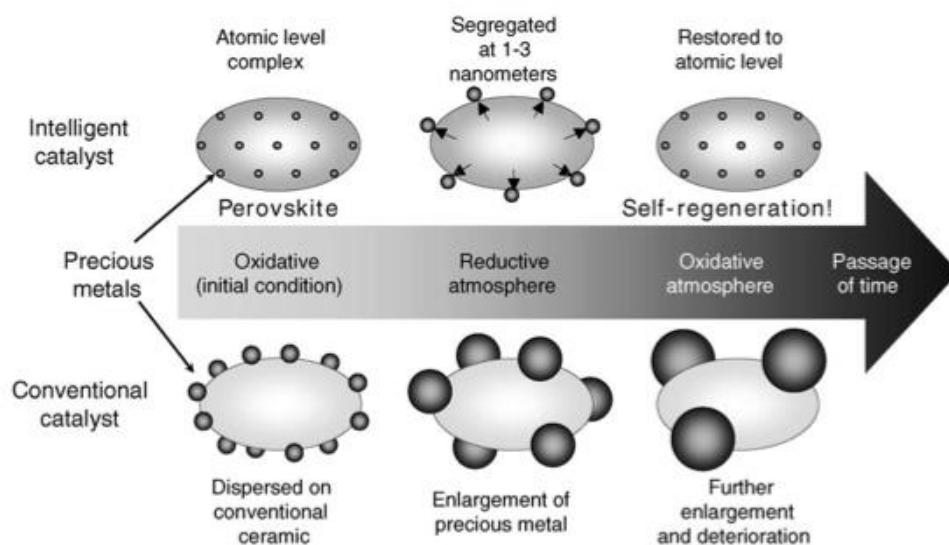


Figure 4. Behavior of the “intelligent” perovskite catalyst and conventional catalyst in redox fluctuations [101]

2.2.3. Sulfur Poisoning of the Perovskite Catalysts

One of the major problems of catalytic converters is the poisoning of the catalyst due to sulfur species such as H_2S , thiophene and COS originating from fuel and engine lubricants. NO_x reduction and storage performances are significantly affected by sulfur leading to deactivation of the catalyst [42]. Perovskite-based catalysts also suffer from sulfur poisoning due to the basic properties of lanthanum, iron, cobalt, etc. [103]. Removal of sulfates at low temperatures is not typically possible and thus the reduction of sulfates requires high temperatures causing deterioration of perovskite lattice [80]. Rossetti et al. [103] investigated the effect of sulfur poisoning on various perovskites of the form $\text{La}_{(1-x)}\text{A}_x\text{BO}_3$ ($(\text{A} = \text{Ce}, \text{Sr})$, $(\text{B} = \text{Co}, \text{Mn}, \text{Fe})$, $(x = 0, 0.1, 0.2)$) with and without Pt or Pd. All of their catalysts showed high activity for methane conversion. First, they examined the effect of the B-site on the methane conversion activity and sulfur poisoning. LaMnO_3 and LaCoO_3 showed the highest activity whereas LaFeO_3 showed the least. The resistance towards sulfur poisoning of the perovskites decreased as follows: $\text{LaMnO}_3 > \text{LaCoO}_3 > \text{LaFeO}_3$. LaMnO_3 , LaCoO_3 and LaFeO_3 lost 10%, 17% and 18% of the original conversion activity, upon poisoning respectively. This behavior was attributed to the higher basicity of Mn among other B site cations. It was suggested that the CO_2 which was generated as the reaction product competes with SO_2 and occupies the Mn sites preventing

sulfur poisoning of the perovskite. In the same study, the effect of A-site substitution on sulfur poisoning of the perovskites were also studied [103]. Up to 10 wt% Sr addition was observed to enhance the activity of the Mn-based perovskites, however further substitution did not affect the performance [103]. For LaCoO_3 , Sr addition led to a slight decrease in the activity. The insertion of Sr to all types of perovskites studied in this work [103] improved resistance towards sulfur poisoning, which was found to be the highest for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$. Sr incorporation also resulted in the creation of oxygen vacancies and an increase in the oxidation state of the B-site cation, thereby increasing the acidity of the metal ion and weakening the SO_2 surface binding. As discussed above, although the presence of Sr improved the sulfur tolerance, this was not the case for Ce^{4+} substitution which had an adverse effect on the poisoning resistance [103]. This study also revealed that the presence of Pd or Pt enhanced the activity of Co-based perovskites. The insertion of Pt increased methane conversion for LaMnO_3 , but Pd diminished the activity. Both Pt and Pd incorporated perovskites showed high resistance against sulfur poisoning. The highest activity was obtained for Pt/LaMnO_3 together with the highest sulfur resistance. Moreover, Koponen et al. [105] showed that extremely high Pd loadings, such as 10 wt% on $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ -type perovskite catalysts increased the resistance against sulfur poisoning, however, higher Pd loadings also led to a decrease in methane conversion. The poisoning mechanism of Al_2O_3 -supported LaCoO_3 was studied by Zhu et al [104]. The reaction between LaCoO_3 and SO_2 was reported to yield $\text{La}_2(\text{SO}_4)_3$, $\text{La}_2(\text{SO}_3)_3$, $\text{La}_2\text{O}_2\text{SO}_4$ and CoO species with the destruction of the perovskite structure. Annealing to higher temperatures was found to help removal of sulfates/sulfites but regeneration of the perovskite structure was reported to be not feasible. Zhang et al. [35] also observed the destruction of the perovskite structure of LaFeCuO_3 via sulfur poisoning. Partial re-construction of the perovskite structure was achieved by exposing the sample to a reducing atmosphere.

CHAPTER 3

3. EXPERIMENTAL

3.1. Sample Preparation

3.1.1. Synthesis of Pd-free LaMnO_3 and LaCoO_3 Perovskite Samples

Perovskite samples were synthesized using the citrate method as prescribed in the recent GM patent [37]. First, citric acid with 10 weight percent excess was dissolved in distilled water. Nitrate precursors of the corresponding metals (see Table 1 for details) were added into the prepared citric acid solution. Solutions were stirred for 1 hr followed by heating at 353 K with continuous stirring under ambient conditions. During heating, the solvent was slowly evaporated and a viscous gel formation was observed concomitant with the evolution of a brown gas (i.e. NO_2). The obtained gel was placed in an oven and heated at 363 K overnight in air. Next, the samples were finely ground in a mortar to obtain a powder form. Finally, obtained powders were calcined in an oven at 873, 873, 1073, and 1173 K for 5 hr in air. The amounts of chemicals used in the synthesis and the corresponding calcination temperatures are listed in Tables 1 and 2, respectively.

3.1.2. Synthesis of Pd-impregnated LaMnO_3 and LaCoO_3 Perovskite Samples

LaMnO_3 and LaCoO_3 samples were synthesized as described in section 3.1.1. Next, perovskite samples were calcined at 973 K for 5 hours in air and then mixed with deionized water and stirred continuously for 1 hour. This is followed by the addition of 1.5 wt% of Pd precursor to the perovskite suspension (i.e. 0.03248 g $\text{Pd}(\text{NO}_3)_2$ for every 1.00 g of perovskite) and stirring for 3 hr. Then, the samples were aged for 1 day under ambient conditions. After aging, a black precipitate was obtained below a clear and colorless solution. Then, the samples were dried overnight at 393 K under ambient conditions. Finally, obtained samples were calcined in air at 773 K for 5 hr. Samples prepared via the impregnation method were denoted as Pd/ LaMnO_3 and Pd/ LaCoO_3 in Tables 1 and 2.

3.1.3. Synthesis of La₂O₃

La₂O₃ was synthesized using La(NO₃)₃.6H₂O(s) precursor calcined at 973 K in an open-air oven for 12 hr.

Table 1. Calcination temperatures of the synthesized samples.

Sample Name	Calcination Temperature (K)
LaMnO ₃	873
LaMnO ₃	973
LaMnO ₃	1073
LaMnO ₃	1173
LaCoO ₃	873
LaCoO ₃	973
LaCoO ₃	1073
LaCoO ₃	1173
1.5wt% Pd/LaMnO ₃	973
1.5wt% Pd/LaCoO ₃	973

Table 2. The amounts of chemicals used in the synthesis.

Precursors	LaMnO ₃	LaCoO ₃	Pd/LaMnO ₃	Pd/LaCoO ₃
La(NO ₃) ₃ .6H ₂ O	1.7905g	1.7613g	1.7905g	1.7613g
Mn(NO ₃) ₃ .4H ₂ O	1.0379g	-	1.0379g	-
Co(NO ₃) ₂ .6H ₂ O	-	1.1838g	-	1.1838g
Pd(NO ₃) ₂	-	-	0.03248g	0.03248g
Citric acid	1.9116g	1.8805g	1.9116g	1.8805g
Distilled water	82.7ml	81.3ml	150ml	150ml

3.2. INSTRUMENTATION

3.2.1 XRD

The powder XRD patterns were recorded using a Rigaku diffractometer, equipped with a Miniflex goniometer and an X-ray source with Cu K α radiation, at $\lambda=1.5418$

Å, 30 kV, and 15 mA. The powder samples were pressed and affixed to standard-sized glass slides and scanned in the 10-80° 2θ range with a scan rate of 0.01 deg. s⁻¹. Diffraction patterns were assigned using Joint Committee on Powder Diffraction Standards (JCPDS) cards supplied by the International Centre for Diffraction Database (ICDD).

3.2.2. N₂ Sorption

The specific surface areas (SSA, m²/g) of the samples were measured by the five-point Brunauer-Emmett-Teller (BET) method [38] via low-temperature isothermal adsorption/desorption of N₂. The samples were degassed under vacuum at room temperature for 1 hr, prior to adsorption measurements in order to outgas the physisorbed moisture. The measurements were performed using a Micromeritics ASAP 2000 gas sorption and porosimetry system.

3.2.3. Raman Spectroscopy

Raman spectra were recorded on a HORIBA Jobin Yvon LabRam HR 800 instrument, equipped with a confocal Raman BX41 microscope, spectrograph with an 800 mm focal length, and a CCD detector. The Raman spectrometer was equipped with a Nd:YAG laser (λ=532.1 nm). During the Raman experiments, the laser power was tuned to 20 mW, measured at the sample position, in order to minimize the sample heating effects. Before the Raman measurements, the powder samples were mechanically dispersed onto a single-crystal Si holder. The incident light source was focused onto the sample by using a 50× objective. The confocal hole and slit entrance were set at 1100 and 200 μm, respectively. The spectrometer was regularly calibrated by adjusting the zero-order position of the grating and comparing the measured Si Raman band frequency with the typical reference value of 520.7 cm⁻¹. All Raman spectra were acquired within 100 - 4000 cm⁻¹ with an acquisition time of 213 s and a spectral resolution of 4 cm⁻¹.

3.2.4. TEM

Transmission electron microscopy (TEM) studies were conducted using a JEOL JEM 2100F field emission scanning/transmission electron microscope. Powders for TEM analysis were prepared through solution-drop method. A mixture of methanol and

powders were dispersed on carbon-coated copper grids and directly examined using bright-field (BF) and high-resolution imaging (HRTEM).

3.2.5. SEM

The morphology, elemental composition, and dispersion of the elements on the surface of the samples were investigated using a scanning electron (SE) microscope, equipped with an EDX detector. SEM and EDX data were acquired using a Zeiss EVO40 environmental SEM that is equipped with a LaB₆ electron gun, a vacuum SE detector, an elevated pressure SE detector, a backscattering electron detector (BSD), and a Bruker AXS XFlash 4010 detector. Samples for SEM and EDX analysis were prepared by grinding the powder samples into fine particles and mechanically dispersing them onto an electrically conductive carbon film which was placed on an aluminum sample holder. No additional coatings or dispersive liquids were used for the SEM and EDX sample preparation. SEM images were obtained using a vacuum SE detector where the electron acceleration voltage of the incident beam was varied within 10-20 kV and the samples were kept typically at $\leq 5 \times 10^{-5}$ Torr inside the SEM. All of the EDX data were collected using an electron acceleration voltage of 20 kV and a working distance of 15 mm. For all of the EDX elemental mapping studies, at least four independent areas of identical dimensions on the same catalyst sample were investigated in order to ensure the reproducibility of the results.

3.2.6. XPS

XPS data were recorded using a SPECS spectrometer with a PHOIBOS-DLD hemispherical energy analyzer and a monochromatic Al K α X-ray irradiation ($h\nu = 1486.74$ eV, 400 W). The powder samples were settled on copper based conducting sticky tape. An electron flood gun was used for charge compensation during the XPS analysis. The flood gun parameters were chosen to be appropriate for binding energy (B.E.) shifts and peak width broadening. The following typical flood gun settings were used during the XPS data acquisition: Electron Energy = 3 eV, Emission Current = 50 μ A.

3.2.7. FTIR

FTIR spectroscopic measurements were carried out in transmission mode in the batch-type catalytic reactor [39] coupled to an FTIR spectrometer (Bruker Tensor 27) and a quadrupole mass spectrometer (QMS, Stanford Research Systems, RGA 200) used for TPD experiments. All FTIR spectra were acquired at 323 K. In the TPD experiments, a linear temperature ramp with a heating rate of 12 K/min was utilized to heat the sample within the range of 323–1023 K. The QMS signals with corresponding m/z were monitored during the TPD measurements. A Hg-Cd-Te (MCT) detector which is used for recording FTIR data works with liquid nitrogen (LN₂) cooling. Gas pressures are controlled by a MKS Baratron absolute pressure transducer. Rotary and turbo pumps are used for evacuation of gases throughout the instrument. During FTIR measurement, the average scan is 128 and resolution is 4 cm⁻¹. A high conductance and lithographically-etched tungsten grid (P/N PW10379-003) is used for pressing the powder samples. About 20 mg samples are pressed on the W-grid. Tantalum foil is spot-welded to the top of the W-grid. The tungsten grid is connected to the copper legs together with a ceramic vacuum feed through. A K-type thermocouple which monitors the temperature is spot-welded to the tantalum foil that already connected to the grid. An adjustable dc power supply and computer controlled PID electronics control the temperature up to 1173 K. After the samples were placed into the batch reactor, it was baked out at 403 K for 12 hours to both remove surface water and bake the chamber walls. Before each experiment, the sample surface is activated by flushing the reactor with 1 Torr NO_x gas for five minutes, then evacuating the NO_x and annealing to 973 K.

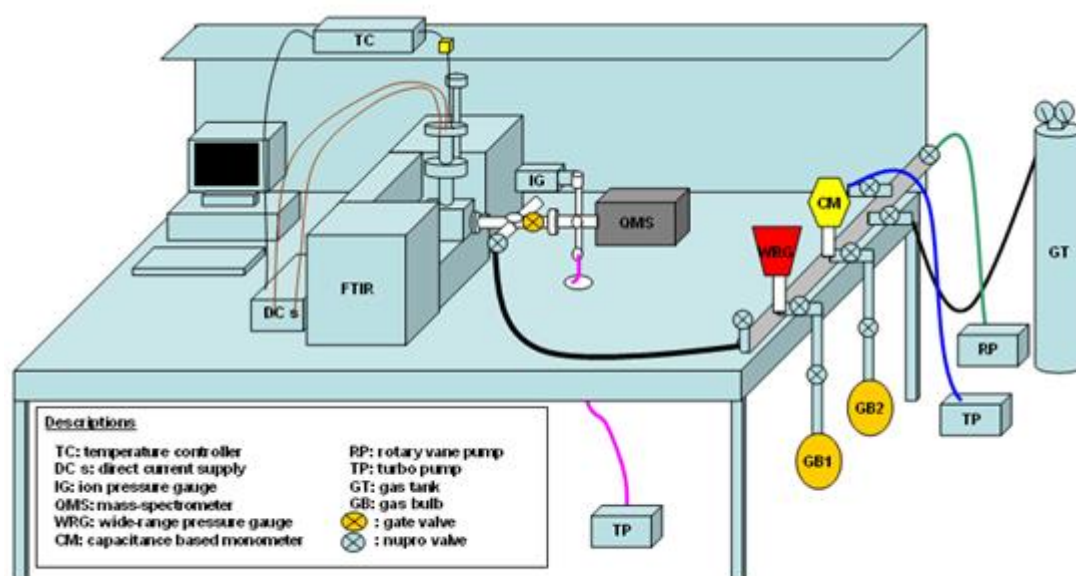


Figure 5. Schematic diagram of in situ FTIR and TPD analysis system [40].

3.2.7.1. Stepwise NO_x (g) Adsorption Experiments

Before the actual NO₂ adsorption experiments, each sample was activated via an initial treatment with NO₂ in order to burn-off residual carbonaceous species followed by annealing at c.a. 900 K in vacuum. These samples are labeled as “activated.” NO₂ (g) was dosed on to the activated surfaces. First, 1 Torr NO₂ (g) was dosed into the manifold and released onto the sample for 1 min. Upon expansion into the spectroscopic reactor, this 1 Torr of NO₂ (g) in the manifold resulted in an NO₂ pressure of 0.1 Torr over the sample. Before taking IR data, NO_x was evacuated until the pressure inside the chamber reached about 10⁻³ Torr. This procedure was repeated 10 times for each sample. Finally, the surface was saturated via dosing with 5 Torr NO₂ over the sample for 10 minutes. For the whole adsorption experiment, the temperature was kept 323 K. NO₂(g) used in the experiments was prepared by mixing NO(g) (Air Products, 99.9%) and O₂(g) (Linde GmbH, Germany, 99.999%) followed by multiple freeze-pump-thaw cycles for further purification.

3.2.7.2. Stepwise NO_x (g) Desorption Experiments

In order to understand the thermal stabilities of adsorbed species, desorption experiments were performed. After saturation of surfaces with 5 Torr NO₂ at 323 K,

the temperature was linearly increased from 323 K to 823 K in order to remove the surface species. While recording the IR spectrum, the sample was cooled to 323 K.

3.2.7.3. NO_x Adsorption over Reduced Surfaces

Perovskite materials were pre-treated with an aggressive reducing agent, H₂(g), before the NO_x adsorption experiments. The surface was reduced with 5.0 Torr H₂(g) at 623 K for 10 minutes. After evacuation of H₂ at 323 K, 5 Torr NO₂ (g) was dosed over the sample for 10 minutes. The IR spectrum was recorded after pumping out the NO₂ (g). These perovskite samples were mentioned as “*reduced*” which refers to the reduction of the material surface with 5.0 Torr H₂(g) at 623 K for 10 minutes prior to NO₂ exposure.

3.2.7.4. SO_x Adsorption Experiments

Sulfation experiments were performed with SO₂+O₂ (which will be hereafter referred as SO_x) gas mixture with a SO₂:O₂ partial pressure ratio of 1:10. Previously activated samples were exposed to 2 Torr SO_x (g) for 10 min at 323 K. After recording the data, the samples were heated between 373-673 K with 100 K increments in the presence of SO_x(g). At each temperature, the samples were cooled down to 323 K for IR data acquisition. The samples were heated up to 1073 K in vacuum where the temperature increment is 100 K between 373-673 K and 200 K between 673-1073 K. All FTIR data were recorded at 323 K.

3.2.7.5. Reduction of SO_x via H₂

Samples were poisoned with 2 Torr SO_x at 673 K for 30 min prior to the reduction process. SO_x was pumped out at 673 K, and the samples were cooled down to 323 K for H₂ dosage. 2 Torr H₂ gas was introduced onto the sample at 323 K and annealing in H₂ atmosphere was performed between 673-973 K with a 100 K increment.

3.2.7.6. NO_x Adsorption Experiments on Poisoned Samples

Poisoning of the samples were performed with 2 Torr SO_x at 673K for 30 minutes. Before cooling the sample to 323 K, SO_x was evacuated. 5 Torr NO₂ (g) was dosed on the sample at 323K for 10 minutes to saturate the poisoned surface with NO_x. Evacuation of NO₂ was followed by IR data acquisition.

3.2.8. Temperature Programmed Desorption (TPD)

TPD experiments were done using a Quadrupole Mass Spectrometer (QMS) that was connected to the vacuum chamber via a pneumatic gate valve. The powder sample of about 20 mg was pressed onto a tungsten grid which was mounted on the IR/TPD cell, as described in section 2.2.7. The oxidation-resistant thoria-coated iridium filament of the mass spectrometer was outgassed for 30 min before each TPD experiment. After cooling to 323 K, 8 Torr of NO₂ for 20 min was dosed onto the sample until equilibrium was reached. To remove weakly physisorbed species, the system was outgassed at 1×10^{-6} Torr. Next, TPD experiments were performed. Thermally desorbed NO_x species during the TPD process were monitored by simultaneously recording the QMS signals with mass to charge ratios (m/z) equal to 18 (H₂O), 28 (N₂/CO), 30 (NO), 32 (O₂), 44 (N₂O/CO₂) and 46 (NO₂). TPD experiments were done within the temperature range between 323-1023 K where the temperature ramp rate was 12 K/min.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. Structural Characterization

4.1.1. XRD Experiments

XRD analysis of the synthesized samples will be discussed in the following sub-sections.

4.1.1.1. XRD Analysis of La_2O_3

The XRD pattern of the synthesized La_2O_3 sample is shown in Figure 6. The XRD pattern reveals the presence of a pure hexagonal La_2O_3 phase (ICDD card no: 00-005-0602) without any other ordered phases (Figure 6).

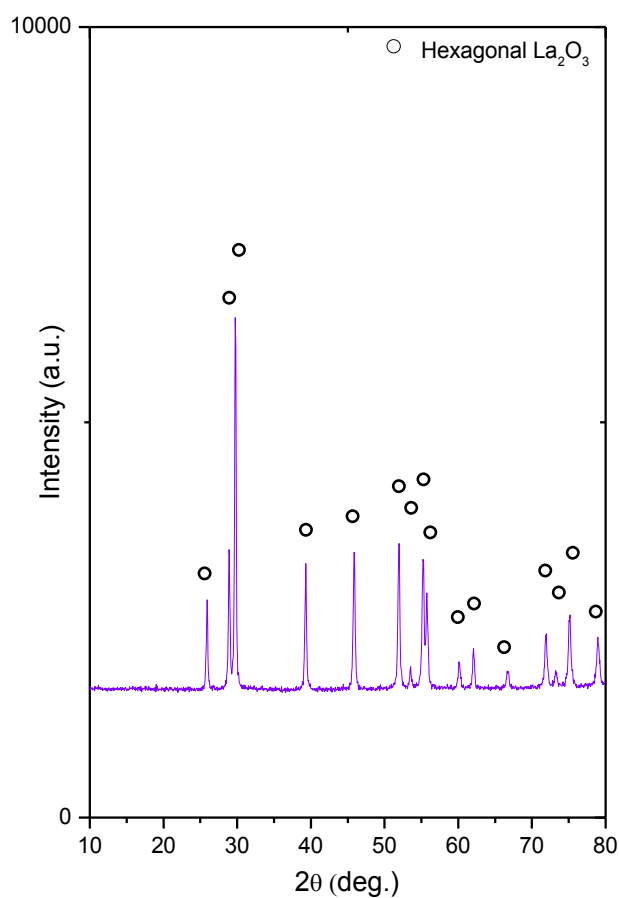


Figure 6. XRD pattern of the synthesized La_2O_3 sample after calcination at 973 K.

4.1.1.2. XRD Analysis of LaCoO₃

XRD patterns of the LaCoO₃ samples obtained after calcination at different temperatures are presented in Figure 7. Figure 8 shows the major diffraction signal appeared at $2\theta = \sim 33^\circ$. After calcination at 873 K, the predominantly existing phase seems to be the cubic perovskite phase (ICDD card no: 01-075-0279). It is apparent that the XRD lines at 873 K are broad and composed of convoluted features indicating the presence of a poorly crystalline rhombohedral perovskite phase (ICDD card no: 00-025-1060) as well as the cubic perovskite phase [42, 43]. At higher calcination temperatures, the perovskite signals become sharper and are better resolved. With increasing calcination temperatures, the major perovskite peak ($2\theta = \sim 33^\circ$) starts to split into a couple of well-resolved signals, corresponding to rhombohedral and cubic perovskite phases (Figure 8). Crystal structures of the cubic and rhombohedral phases are shown in Figure 9 [102].

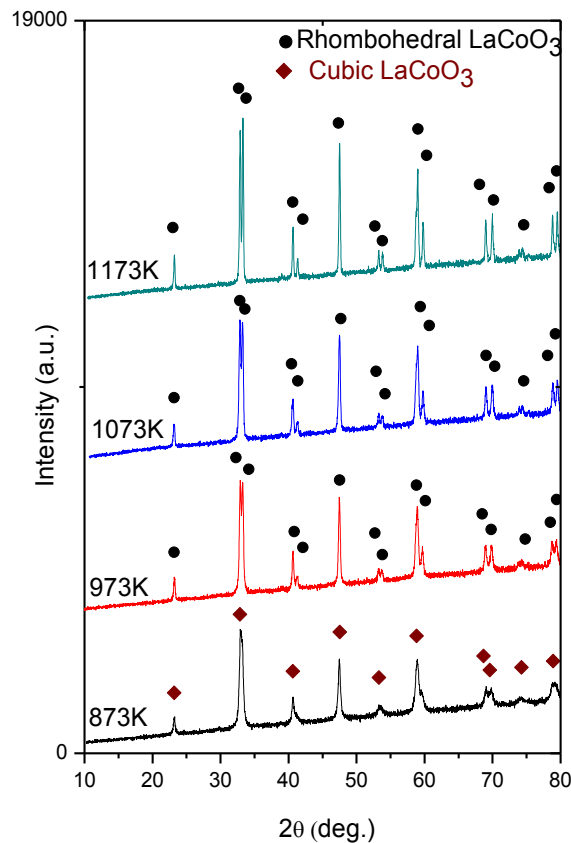


Figure 7. XRD patterns of the synthesized LaCoO₃ samples after calcination at different temperatures.

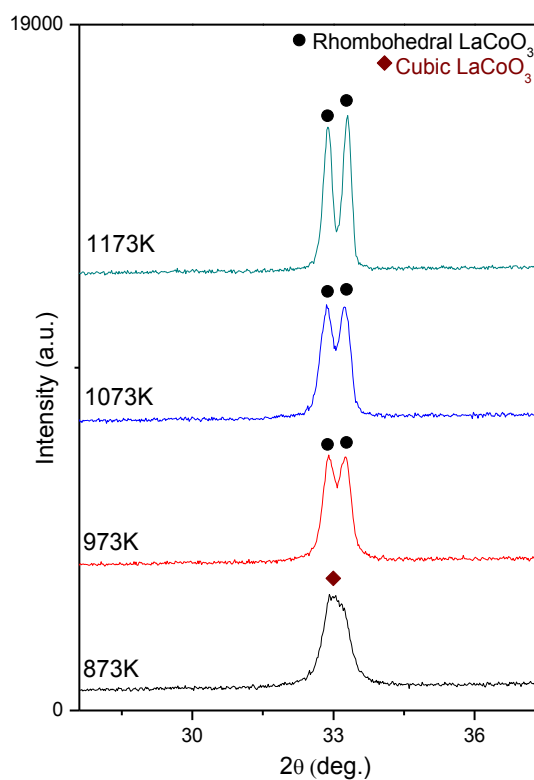


Figure 8. Characteristic XRD signals corresponding to the cubic and rhombohedral LaCoO₃ samples.

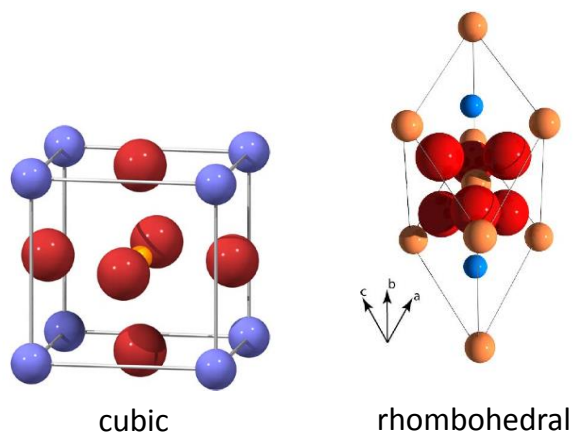


Figure 9. Cubic and Rhombohedral structures of LaCoO₃ [102]

4.1.1.3. XRD Analysis of LaMnO₃

As in the case of the LaCoO₃ samples, no other oxide phases were detected in the XRD analysis of the LaMnO₃ samples other than the perovskite phases (Figure 10). It is worth mentioning that Mn-based samples are amorphous at 873 K and start to

crystallize at higher temperatures ($T > 873$ K). Figure 11 indicates the major diffraction pattern of LaMnO_3 appeared at $2\theta = \sim 32.8^\circ$. After calcination at 973 K, a cubic perovskite phase (ICDD card no: 00-051-1516) is formed as can be seen in Figure 11. As the calcination temperature is increased to 1073 K, cubic to rhombohedral perovskite (ICDD card no: 01-073-5958) phase transformation is observed with splitting of the signal [43, 44]. The major perovskite signal, which is relatively convoluted at low temperatures splits into a doublet at higher calcination temperatures, indicating the formation of a well-ordered rhombohedral phase at higher temperatures (Figure 11).

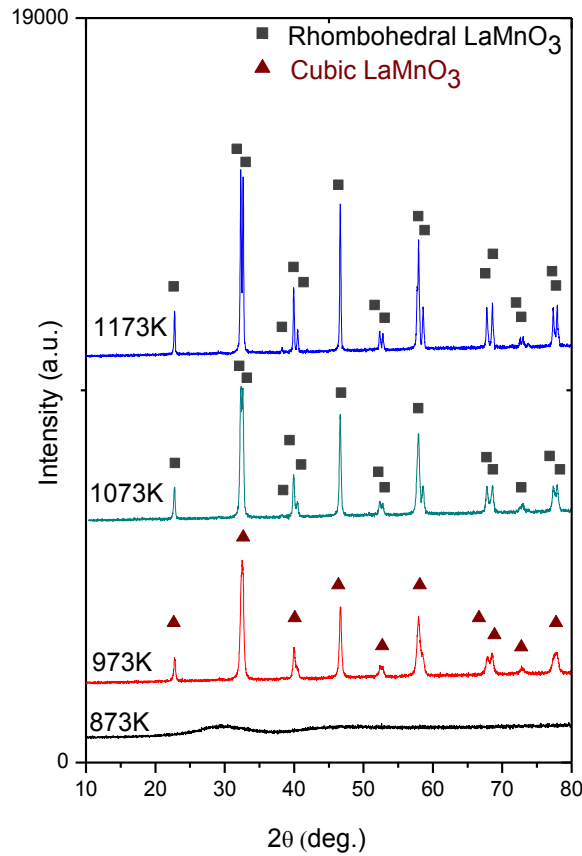


Figure 10. XRD patterns of the synthesized LaMnO_3 samples after calcination at different temperatures.

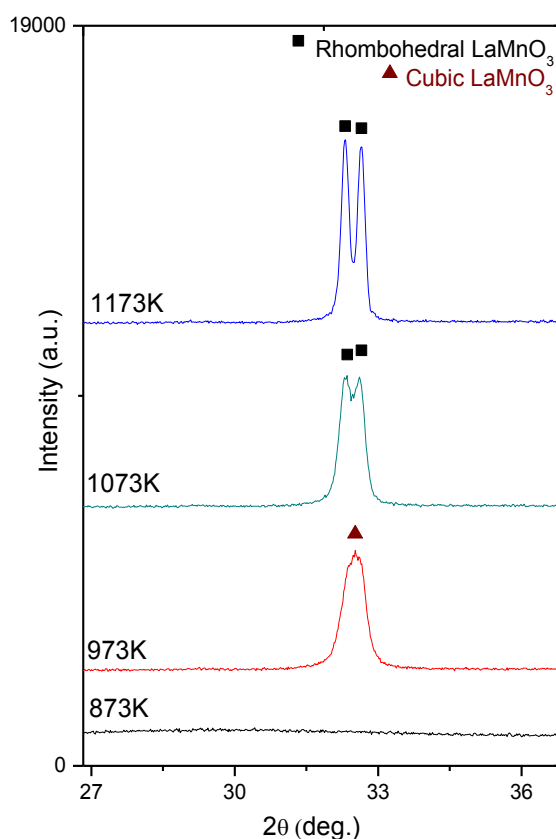


Figure 11. Characteristic XRD signals corresponding to the cubic and rhombohedral LaMnO₃ samples.

4.1.1.4. XRD Analysis of Pd/LaMnO₃ and Pd/LaCoO₃

Samples synthesized using the Pd impregnation protocol were also analyzed via XRD (Figure 12). These samples were calcined at 973 K. For both of the Pd-impregnated samples, the only detectable phases were perovskite phases and no other ordered oxides such as PdO were observed. While Mn-based perovskite structures have only a single peak related to the cubic lattice (with a possible contribution from a poorly crystallized rhombohedral phase), the major diffraction line of Co-based perovskites is split into two peaks which exhibits the transformation from cubic to rhombohedral structure (Figure 13).

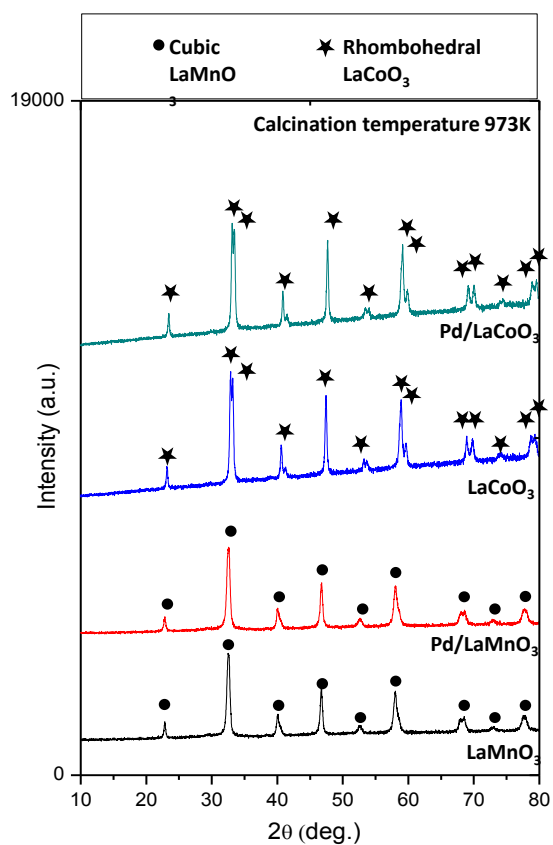


Figure 12. XRD patterns of LaMnO₃ and LaCoO₃ after calcination at 973 K and their Pd impregnated counterparts. (Pd impregnated samples were additionally calcined at 773 K after impregnation).

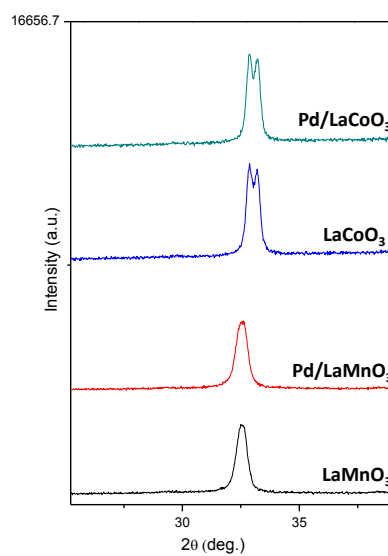


Figure 13. Characteristic perovskite XRD signals corresponding to the Pd-free and Pd-containing perovskite samples calcined at 973 K

4.1.2. Raman Spectroscopy Experiments

As a benchmark measurement, the Raman spectrum of a pure La_2O_3 sample which was synthesized as described above was also acquired (Figure 14). As expected, the corresponding Raman spectrum displayed three characteristic La_2O_3 Raman peaks located at 95, 181 cm^{-1} with the most intense feature appearing at 401 cm^{-1} .

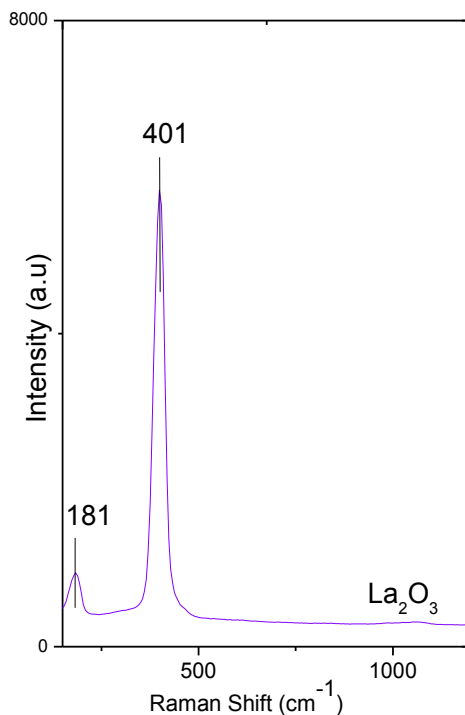


Figure 14. Raman spectrum of La_2O_3 benchmark sample.

Raman spectra of LaMnO_3 and LaCoO_3 are presented in Figures 15 and 16. The Raman spectra of perovskites demonstrate a convoluted set of peaks. After calcination at 973 K, the LaMnO_3 sample reveals Raman shifts at c.a. 72, 194, 410, 644 and 1022 cm^{-1} (Figure 15). These bands can be tentatively assigned as follows, the band at 410 cm^{-1} is most likely associated with the La-O modes since the La_2O_3 benchmark sample has a major Raman shift at around 401 cm^{-1} . These La-O species can possibly be attributed to both La_2O_3 and LaMnO_3 structures suggesting the presence of La_2O_3 domains on the surface, which may be difficult to detect in XRD, possibly due to their small crystallite size or their lack of atomic order. Additional support for the presence of La-rich phases (i.e. La_2O_3) on the synthesized perovskite surfaces will also be presented in the next sections. The Raman band appearing at

644 cm^{-1} in Figure 15 can be attributed to Mn-O stretchings in accordance with Li et al. [6] who reported a similar peak at 654 cm^{-1} for Mn_3O_4 samples and Ammundsen et al. [7] who also reported a Raman band at 647 cm^{-1} for MnO_2 samples. Moreover, Giraudon et al. published a Raman spectrum of Pd/LaMnO_3 which had only a single peak at 653 cm^{-1} [8]. The remaining Raman bands observed in Figure 15 at around 194 and 1022 cm^{-1} can be assigned to metal nitrates such as Mn-NO_3 .

For the LaCoO_3 samples calcined at 973 K, Raman shifts was observed at around 72, 147, 406, 616 and 1025 cm^{-1} (Figure 16). As discussed above, the 406 cm^{-1} feature can be assigned to La-O species. Giraudon et al. reported a single Raman band appearing at 398 cm^{-1} for Pd/LaCoO_3 and assigned this band to La_2O_3 impurities [8]. Tang et al. investigated the Raman spectra of different cobalt-containing compounds such as CoOOH , Co_3O_4 and CoO ; and observed a sharp feature at c.a. 650 cm^{-1} [9]. Thus it is likely that the feature at 616 cm^{-1} in Figure 16 is associated with Co-O species. Raman bands at around 147 cm^{-1} and 1025 cm^{-1} are assigned to $\text{Co(NO}_3)_2$ [10].

It is worth mentioning that for both Co and Mn based perovskites, no significantly discernible changes were observed in the Raman spectra after Pd doping (Figures 15 and 16).

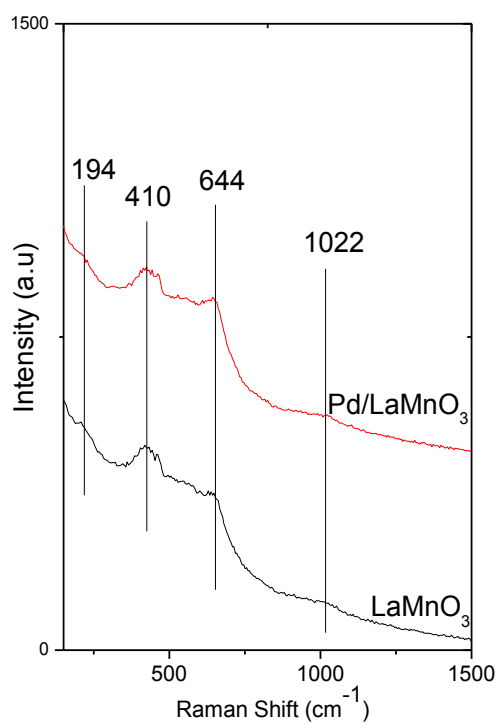


Figure 15. Raman spectra of LaMnO_3 and Pd/LaMnO_3 samples after calcination at 973 K.

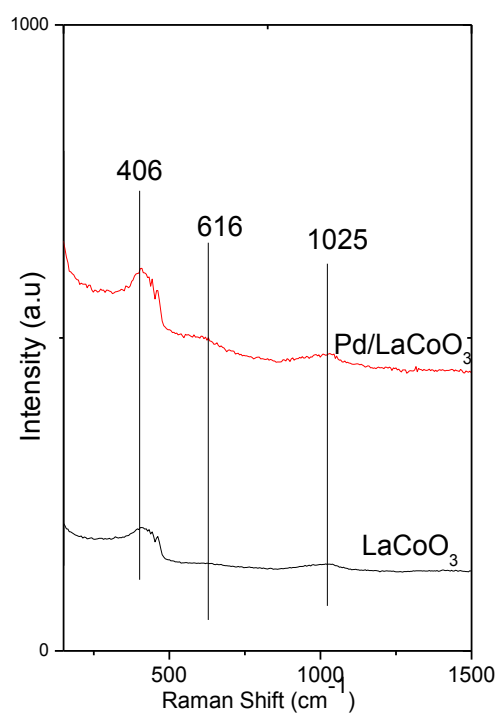


Figure 16. Raman spectra of LaCoO_3 and Pd/LaCoO_3 samples after calcination at 973 K.

4.1.3. N₂ Sorption

The results of the BET specific surface area (SSA) measurements of the synthesized materials are presented in Table 3.

Table 3. BET specific surface areas (obtained after calcination at 973 K)

Sample	Specific BET surface area (m ² /g)
LaMnO ₃	20.64 ± 0.09
LaCoO ₃	7.10 ± 0.01
1.5 wt% Pd/LaMnO ₃	21.90 ± 0.07
1.5 wt% Pd/LaCoO ₃	8.93 ± 0.01

The Mn-based samples calcined at 973 K have relatively high specific surface areas which are approximately around 20 m²/g. On the other hand, SSAs of Co-based samples are about 8 m²/g. Temperature-dependent XRD results clearly indicate that Mn containing perovskites crystallize at higher temperatures. Therefore, it is expected that Mn-based perovskites are less ordered than their Co-based counterparts at 973 K, revealing higher SSAs. Moreover, palladium addition causes minor increase in the SSA (c.a. 2m²/g) for both Mn- and Co- based perovskites within an experimental error.

4.1.4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Mapping Analysis

Figures 17, 18, 19, and 20 illustrate SEM/EDX images that belong to LaMnO₃, LaCoO₃, Pd/LaMnO₃, and Pd/LaCoO₃ samples, respectively. Due to the low lateral spatial resolution and large analysis depth of the SEM instrument used in the analysis, EDX data consists of pixels with x-y dimensions of c.a. 1μm x 1μm. SEM/EDX results of the Pd-free perovskite samples (Figures 17 and 18) suggest the presence of mostly homogeneously distributed La+Mn or La+Co signals. However one can also notice minority areas that seem to be enriched with La. Although this observation is not entirely conclusive, it is in line with the arguments discussed above regarding the presence of La₂O₃ domains (and possibly CoO_x and MnO_x domains) on the perovskite surfaces.

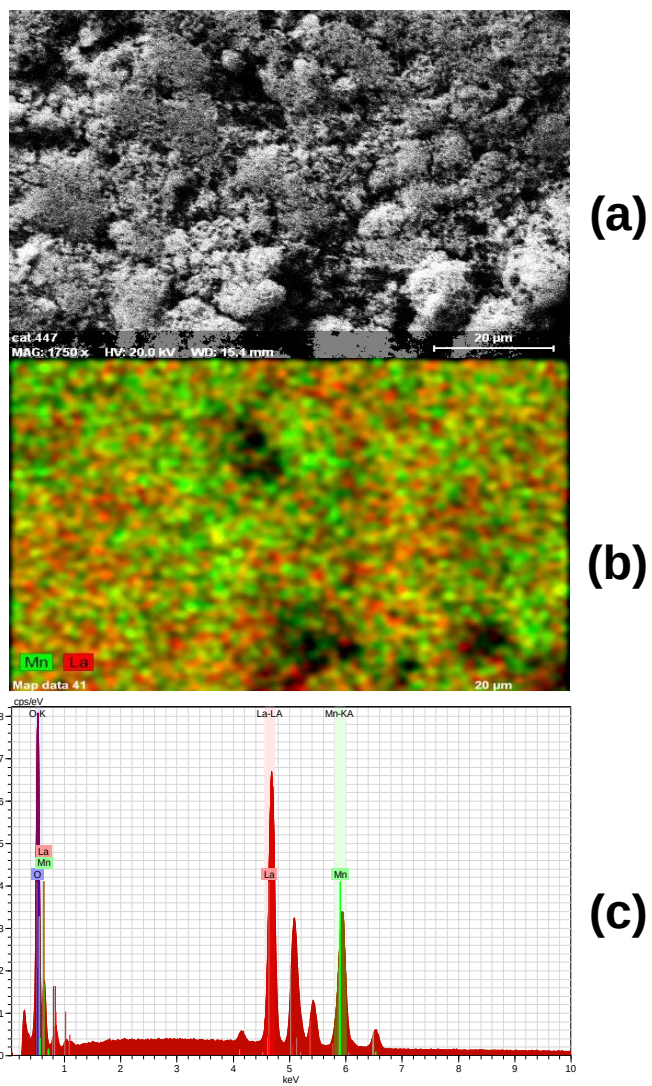


Figure 17. (a) SEM image, (b) La + Mn EDX elemental map and (c) a representative EDX spectrum of LaMnO₃ sample calcined at 973K.

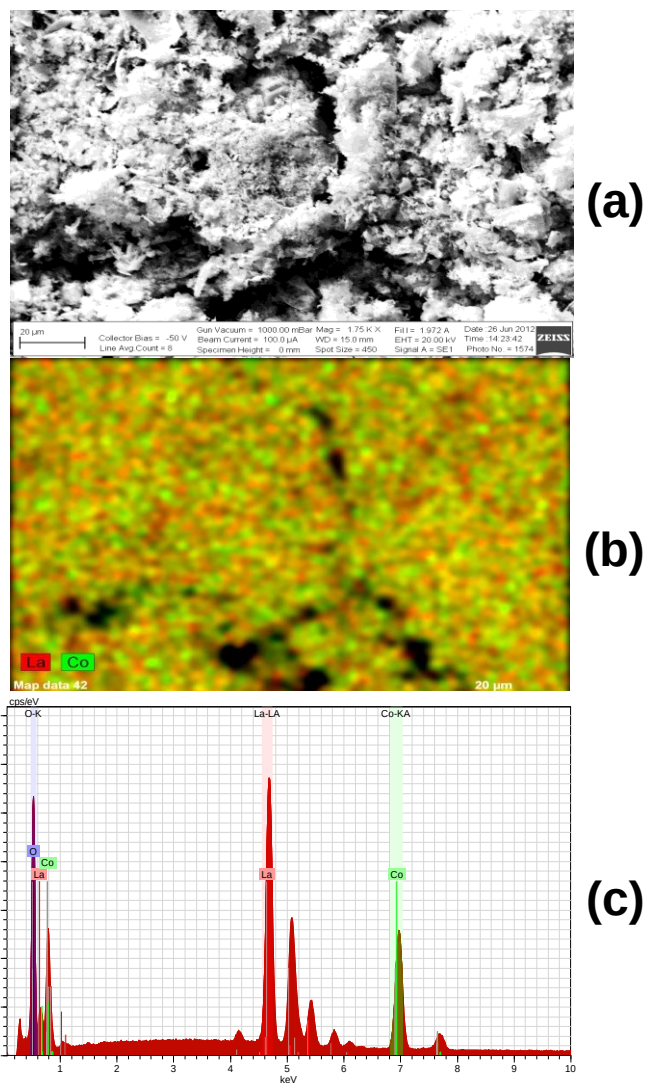


Figure 18. (a) SEM image, (b) La + Co EDX elemental map and (c) a representative EDX spectrum of LaCoO₃ sample calcined at 973K.

SEM/EDX analysis of the Pd-impregnated perovskite samples (Figures 19 and 20) reveal similar La+Mn and La+Co spatial distributions. These samples also display a rather homogenous Pd distribution. The presence of Pd atoms in these samples is clearly evident in the corresponding representative EDX spectra given in Figures 19 and 20.

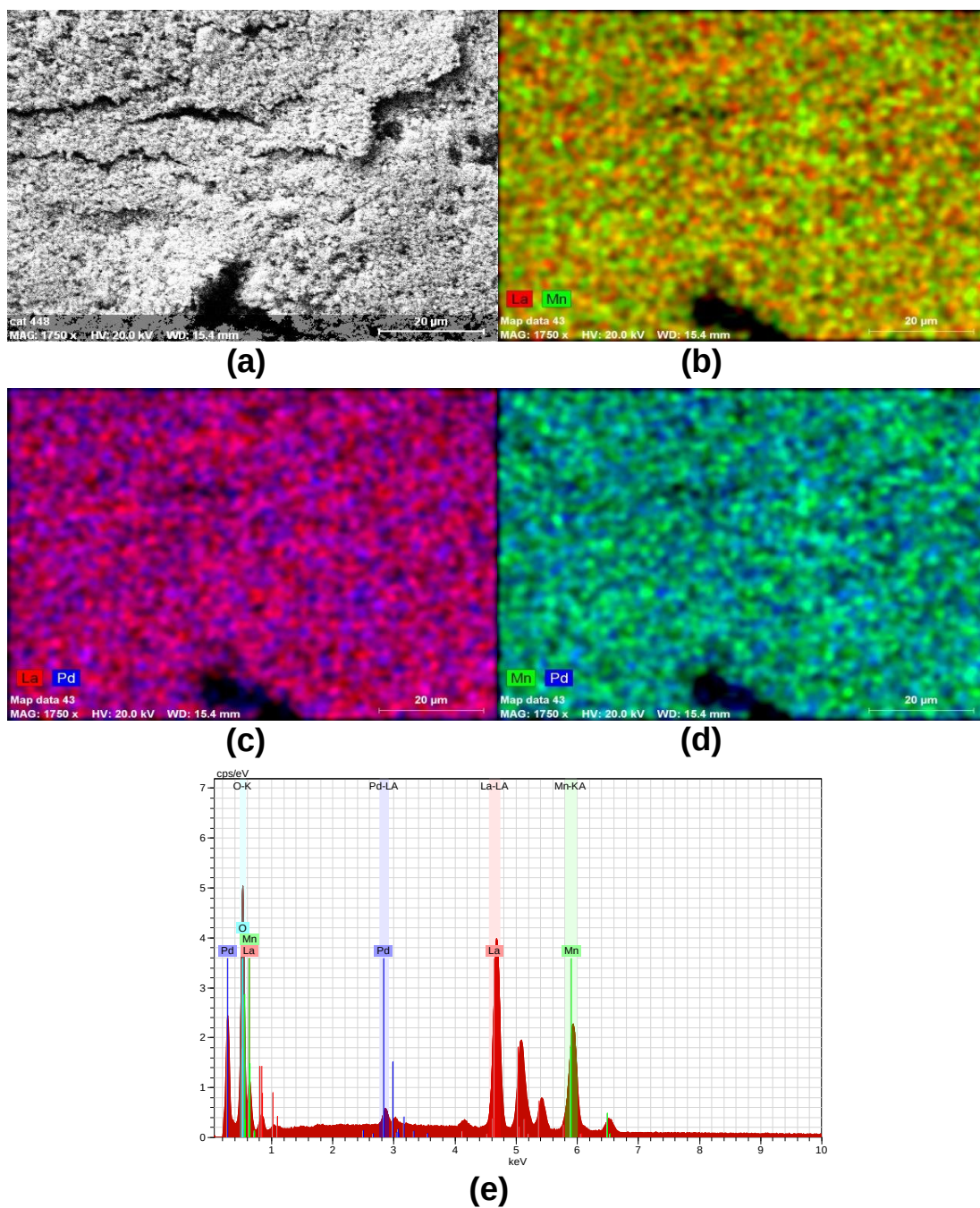


Figure 19. (a) SEM image, (b) La + Mn, (c) La + Pd, (d) Mn+Pd EDX elemental maps and (e) a representative EDX spectrum of Pd/LaCoO₃ sample calcined at 973K.

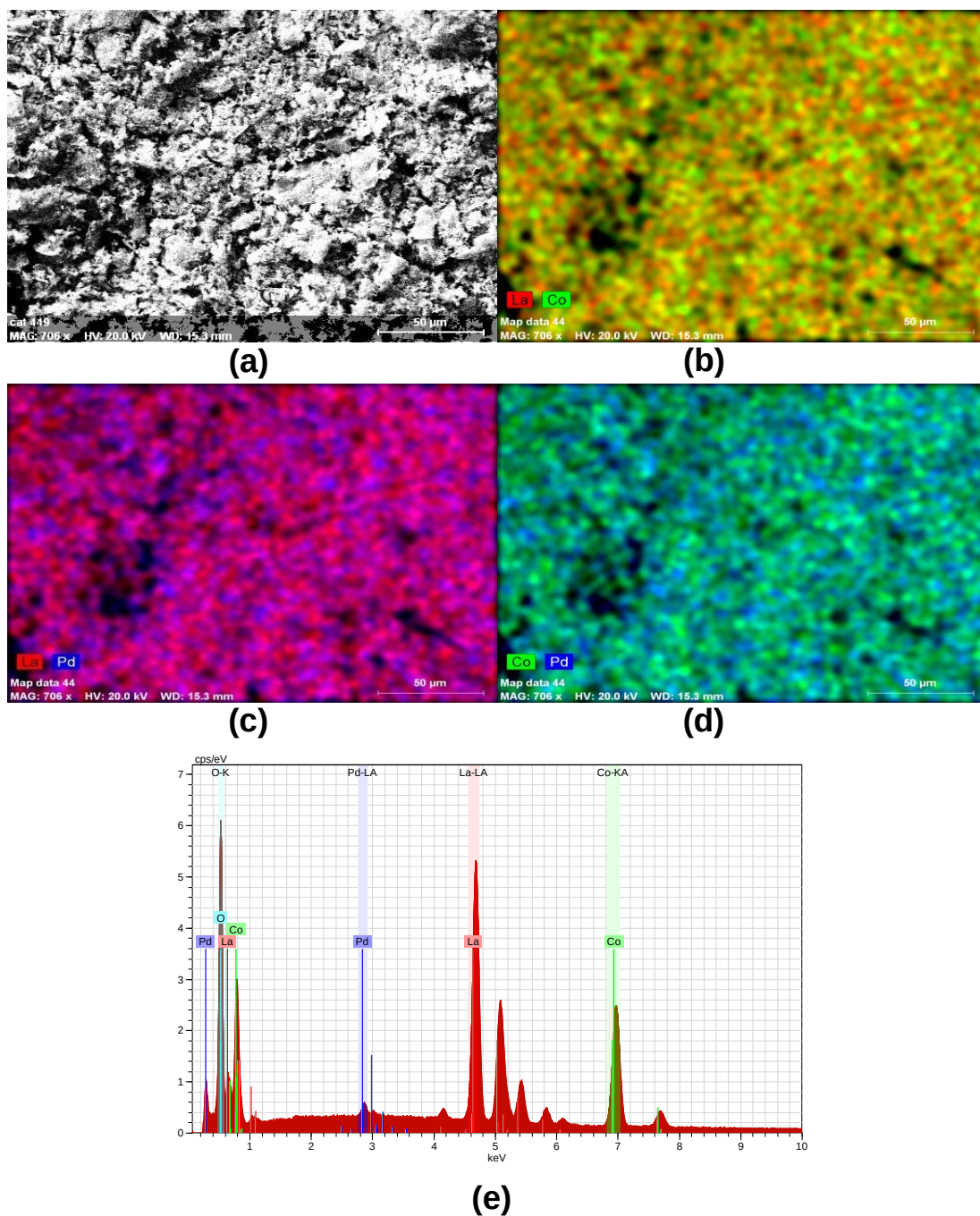


Figure 20. (a) SEM image, (b) La + Co, (c) La + Pd, (d) Co+Pd EDX elemental maps and (e) a representative EDX spectrum of Pd/LaCoO₃ sample calcined at 973K.

4.1.5. Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray (EDX) Analysis

The bright field (BF) and high-resolution TEM (HRTEM) images of the LaCoO₃ sample calcined at 973 K are presented in Figure 21. The BF image (Fig.21 (a)) shows a distribution of several LaCoO₃ particulates. The size of individual

particulates is on the order of 10-20 nm. The SAED pattern obtained from a relatively large area reveals that groups of LaCoO_3 particulate show polycrystalline structure, on the other hand HRTEM image of a single LaCoO_3 particulate reveals the single crystalline nature of the structure (Fig.21 (b)).

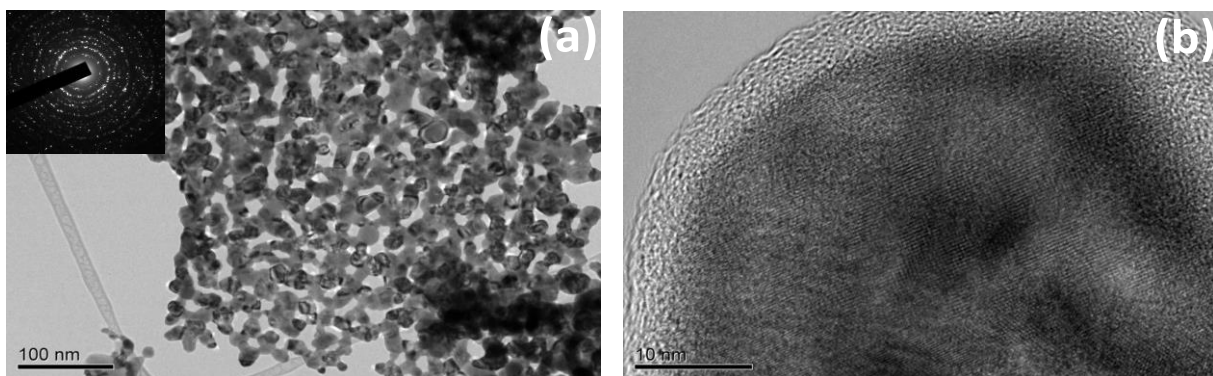


Figure 21. (a) Bright field TEM image showing LaCoO_3 particulates with selected area diffraction pattern (inset) and (b) HRTEM image from a single LaCoO_3 particulate

The BF TEM images corresponding to LaMnO_3 which was calcined at 973 K is shown in Figure 22. As in the case of LaCoO_3 , the size of the particles for Mn-counterpart is about 10-20 nm.

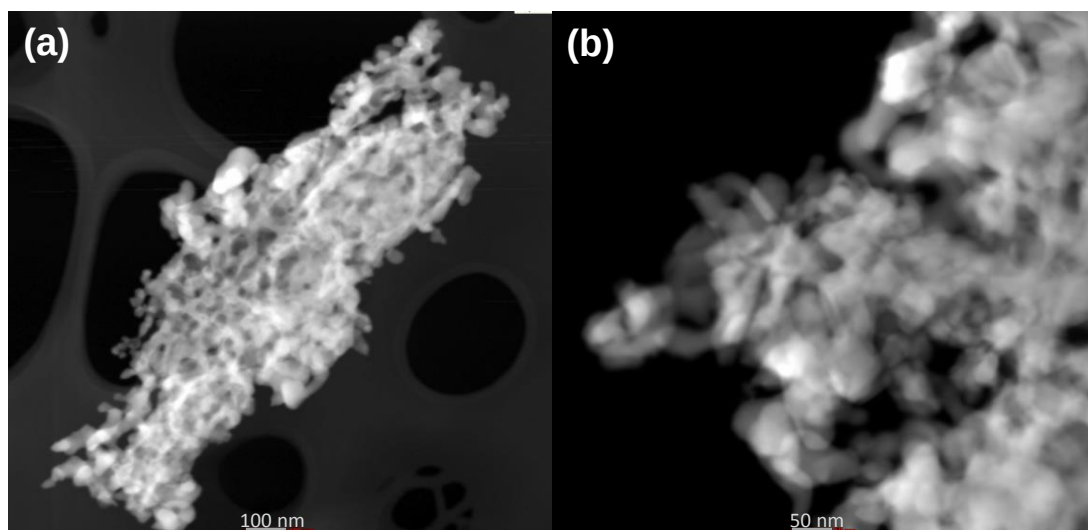


Figure 22. Bright field TEM images showing LaMnO_3 particulates

BF images of Pd/LaCoO₃ and Pd/LaMnO₃ are presented in Figure 23 and Figure 24. Moreover, Figure 25 shows the HRTEM images for Pd/LaMnO₃. In these images, Pd particles are seen to be well-dispersed without aggregating throughout the perovskite surface with an average palladium particle size of 4-5 nm. Lack of any metallic Pd or PdO phases in the XRD measurements discussed in section 4.1.1.4 is consistent with the small Pd particle sizes (i.e. c.a. 5 nm) observed in TEM.

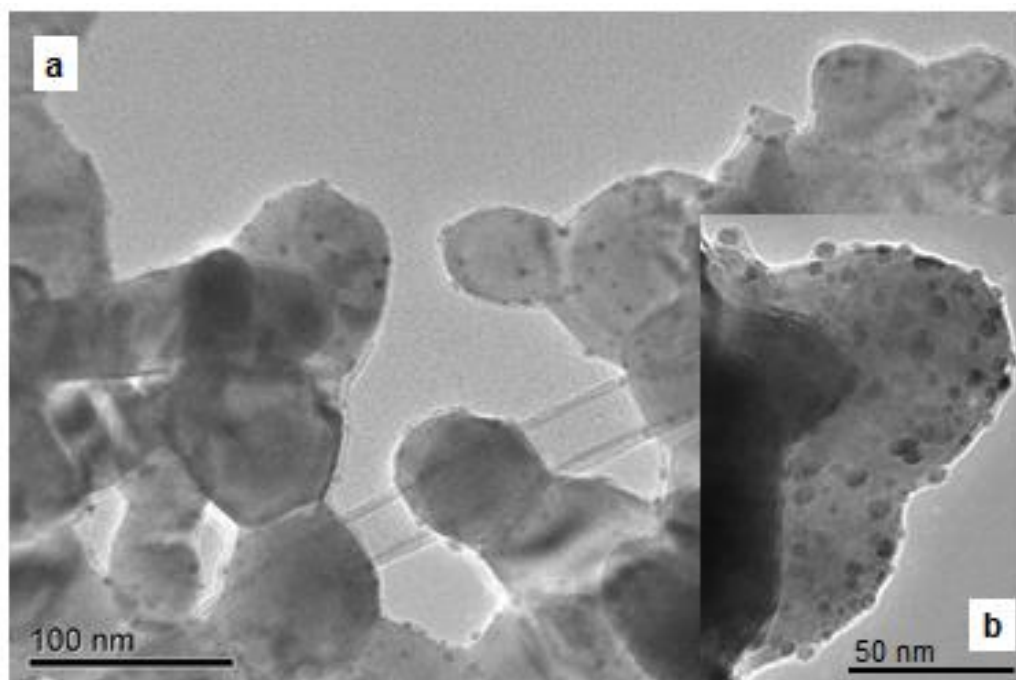


Figure 23. Representative BF TEM image of Pd/LaCoO₃.

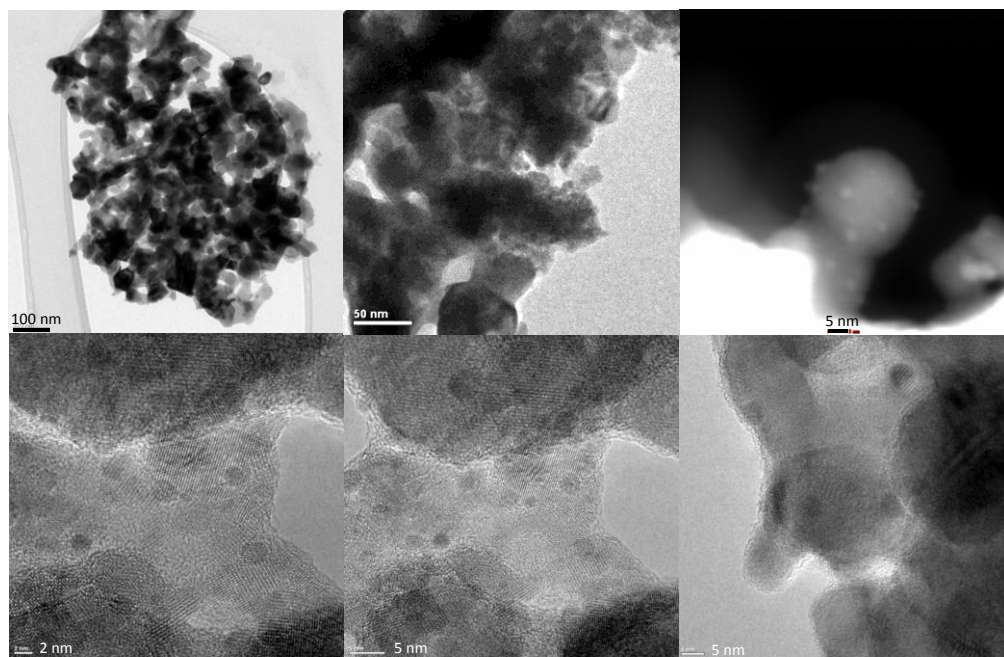


Figure 24. Representative BF TEM images of Pd/LaMnO₃.

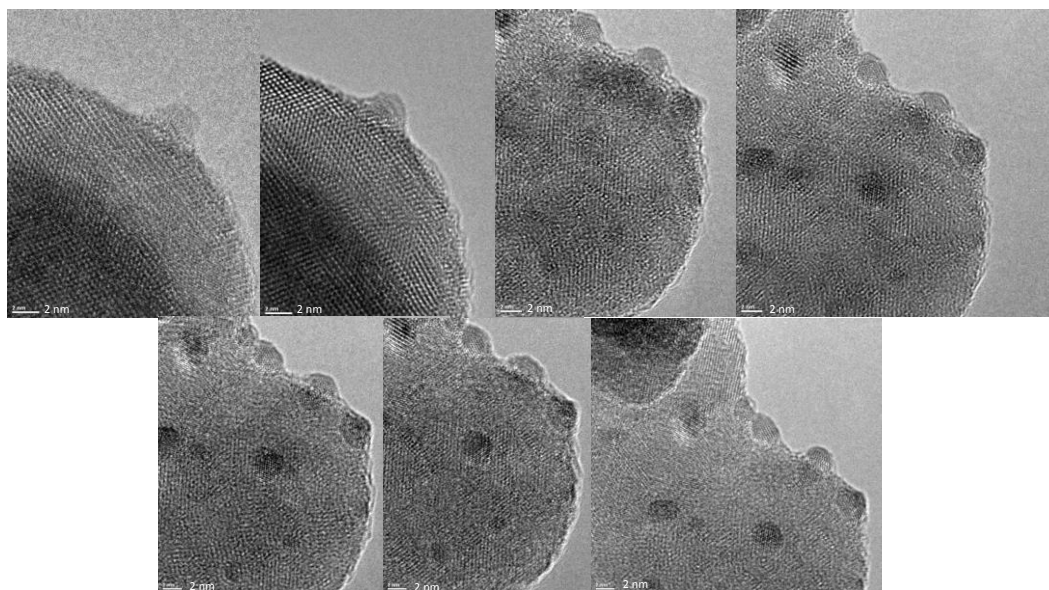


Figure 25. HRTEM image of Pd/LaMnO₃.

4.1.6. X-Ray Photoelectron Spectroscopy (XPS) Analysis

The Pd3d regions of the XP spectra (Figure 26) corresponding to Pd-containing samples demonstrated a 3d doublet with a 5.25 eV splitting. The binding energy (BE) of the Pd3d_{5/2} peak is observed at 336.7-337.0 eV for all of these samples, indicating the presence of an oxidized form of Pd (i.e. Pd²⁺). Metallic Pd which is characterized

by BE ($\text{Pd}3d_{5/2}$) ~ 335.3 eV was not detected on the surface of the investigated samples.

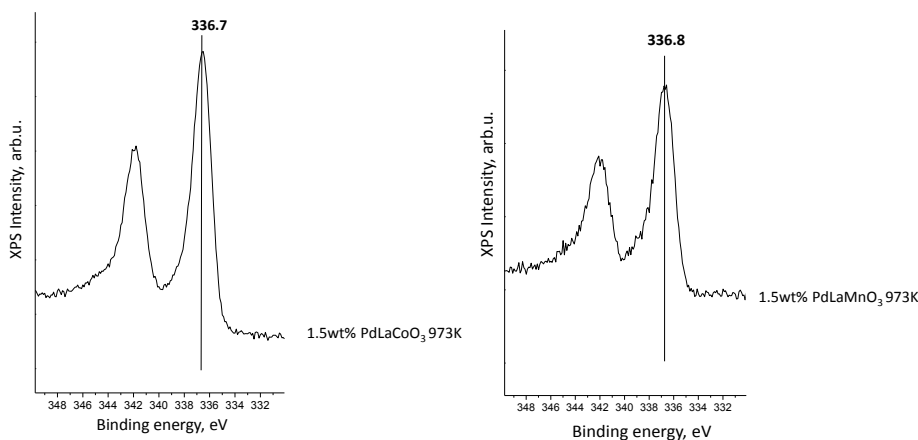


Figure 26. Pd3d XP spectra corresponding to a selected set of synthesized samples calcined at 973 K

The La 4d regions of the XP spectra (Figure 27) of all samples can be deconvoluted by using two doublets with a 3.0 eV of spin-orbital splitting. The narrower doublet with a La $4d_{5/2}$ BE of ~ 101.0 eV for Co-samples and ~ 101.7 eV for Mn-samples can be associated with La^{3+} species located in the perovskite structure. The broader doublet with a La $4d_{5/2}$ BE ~ 103.5 eV for Co-samples and ~ 104.5 eV for Mn-samples may be associated with the overlapping signals originating from lanthanum oxide, lanthanum hydroxide and/or lanthanum carbonate species.

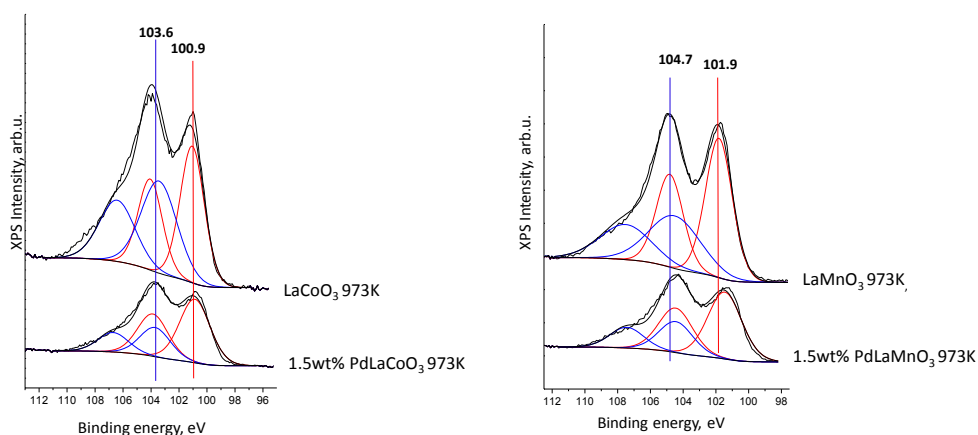


Figure 27. Representative La4d XP spectra corresponding to LaCoO_3 , LaMnO_3 Pd/LaCoO_3 and Pd/LaMnO_3 samples calcined at 973 K

The Co2p_{3/2} spectra (Figure 28) reveal itself in the form of a major asymmetric peak located at 779.8 eV which can be assigned to Co²⁺ and/or Co³⁺ states. The 789.0 eV satellite which is characteristic of Co³⁺ ions [11] supports the presence of Co³⁺ in both Pd/LaCoO₃ and LaCoO₃.

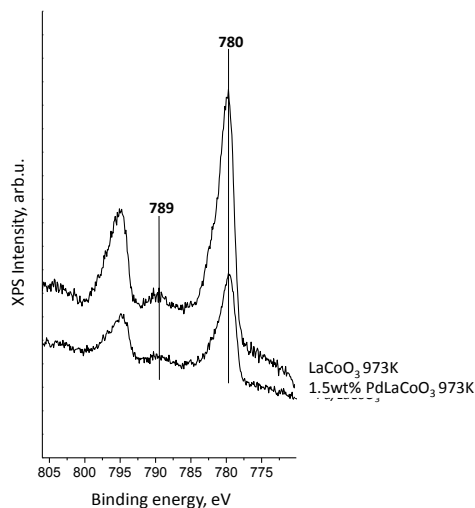


Figure 28. Co2p XP spectra of Co-containing samples calcined at 973 K

Figure 29 presents Mn2p spectra of the selected samples with a major signal appearing at ~ 641.5 eV. It should be noted that due to the closely separated BE values of Mn species corresponding to different oxidation states and the extremely broad Mn2p_{3/2} experimental signals, it is not practically feasible to deduce Mn oxidation state information regarding the analyzed samples.

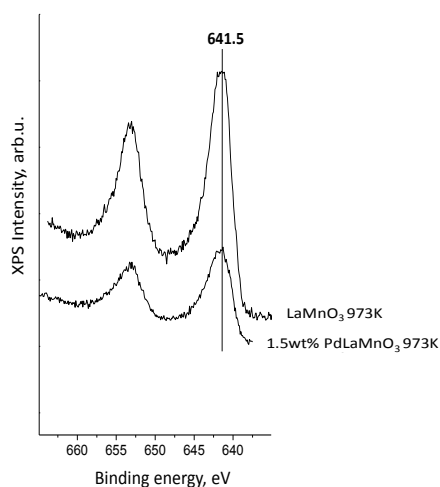


Figure 29. Mn2p XP spectra of Mn-containing samples calcined at 973 K

The C1s spectra of the selected samples (Figure 30) reveal a main peak (amorphous carbon), which was adjusted to 284.6 eV and used as an internal standard for calibration of other XPS signals. The additional peaks in the C1s spectra at ~ 288.7 eV can be assigned to surface carbonates. The relative quantity of the surface carbonates can be estimated from the atomic ratio data presented in Table 4.

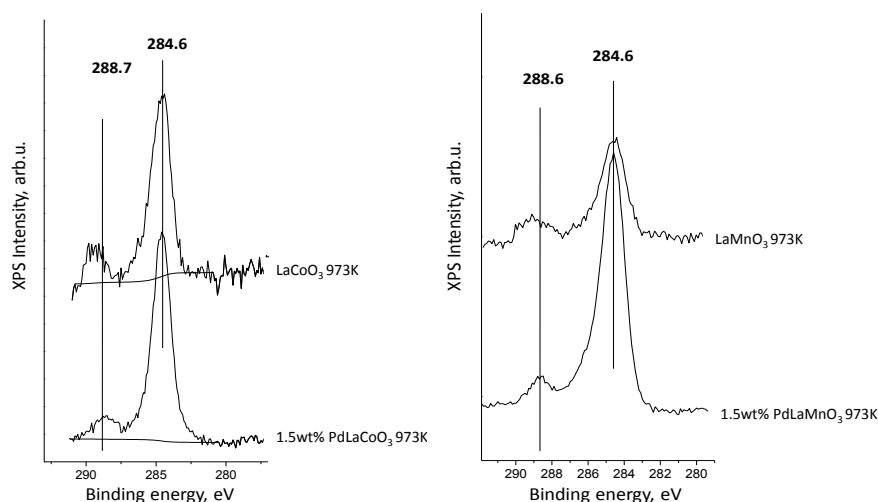


Figure 30. Representative C1s XP spectra of LaCoO₃, LaMnO₃ Pd/LaCoO₃ and Pd/LaMnO₃.

As can be seen from O1s spectra of the selected samples (Figure 31), there are two major features with BE values located at 528.5 eV and 531-532 eV. The former feature can be ascribed to the lattice oxygen of the perovskite structure while the latter can be assigned to adsorbed oxygen species [12, 13] and/or to oxides/hydroxides/carbonates, which are present on the surface. The ~ 533.5 eV shoulder is likely associated with residual nitrates originating from the metal nitrate precursors used in the synthesis that remained on the surface after calcination.

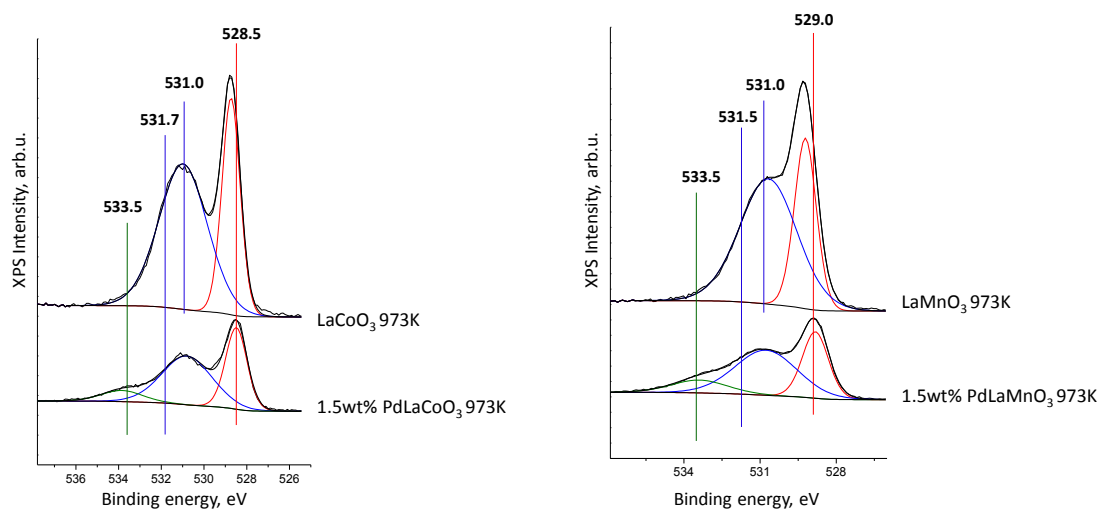


Figure 31. Representative O1s XP spectra of selected samples.

Table 4. BE values (in eV) for the main signals observed in the XP spectra

Sample	Pd3d _{5/2} (PdO)	La3d _{5/2}	La4d _{5/2}	Co2p _{3/2}	Co3p	Mn2p _{3/2}	O1s
LaCoO ₃ 973K	-	833.0	100.7 102.9	779.5	60.6	-	528.4 530.9
LaMnO ₃ 973K	-	833.2	101.7 104.2	-	-	640.7	527.3 528.7
Pd/LaCoO ₃ 973K	336.6	833.4	100.9 103.7	779.7	60.3	-	528.5 530.8
Pd/LaMnO ₃ 973K	336.8	833.9	101.5 104.4	-	-	641.7	528.8 530.8

Table 5. Relative surface atomic ratios of the elements investigated in the XPS analysis of the synthesized samples

Sample	Pd/La	Co/La	C _{carbonate} /La	O _{528.5} /La
LaCoO ₃ 973K	-	0.50	0.31	1.26
1.5wt% Pd/LaCoO ₃ 973K	0.33	0.58	2.73	1.58
Sample	Pd/La	Mn/La	C _{carbonate} /La	O _{529.0} /La
LaMnO ₃ 973K	-	0.60	0.32	0.85
1.5wt% Pd/LaMnO ₃ 973K	0.17	0.65	0.54	1.48

The XPS analysis reveals critical aspects associated with the structural differences between the samples. Firstly, Pd was found to be in Pd²⁺ state on the surface of all Pd containing samples, excluding the existence of metallic Pd species. Relative surface atomic ratios given in Table 5 also clearly indicate that surfaces of all samples are enriched in La, suggesting the presence of La₂O₃, La(OH)_x or La₂(CO₃)_x surface species. Along these lines, Co/La and Mn/La surface atomic ratios are less than one (c.a. 0.5) illustrating that surfaces of the perovskite samples have excess La.

4.2. In-situ Spectroscopic Characterization of the Synthesized Samples under Reactive Conditions

4.2.1. Fourier Transformed Infrared (FTIR) and Temperature Program Desorption (TPD) Experiments

4.2.1.1. NO_x Adsorption and Desorption Behavior of Pd-free Perovskite Surfaces

The FTIR spectra obtained after NO₂ (g) adsorption (successive 0.1 Torr × 1 min NO₂ exposure steps with a final saturation exposure of 5.0 Torr x 10 min) on LaMnO₃ and LaCoO₃ at 323 K are shown in Figure 32a and Figure 32b, respectively. Before the adsorption experiments, each sample was treated with NO₂ followed by annealing at c.a. 900 K in vacuum. These samples are labeled as “*activated*” in the figure legends. The general aspect of the vibrational spectra corresponding to both LaMnO₃ and LaCoO₃ surfaces bear significant resemblance to each other, revealing similar types of adsorbed NO_x species. The major IR frequencies in Figure 32 located at 1649 cm⁻¹

and 1009 cm^{-1} are assigned to asymmetric and symmetric stretching modes of bridging nitrate species on the perovskite surfaces, respectively [14]. As compared to LaCoO_3 , these modes of bridging nitrate are more pronounced for LaMnO_3 . Monodentate nitrates is another type of oxygen-coordinated nitrates which are located at 1530 cm^{-1} and 1269 cm^{-1} in the IR spectra. IR features located at 1568 cm^{-1} and 1246 cm^{-1} correspond to bidentate nitrates appearing on the surface [15, 16]. Nitrito species are located between $1485\text{--}1400\text{ cm}^{-1}$ ($\nu_{\text{N=O}}$), $1365\text{--}1075\text{ cm}^{-1}$ ($\nu_{\text{N-O}}$) and $840\text{--}820\text{ cm}^{-1}$ (ν_{ONO} , bending) in the IR analysis [17-20] so IR bands at 1487, 1430, 1321 and 839 cm^{-1} belong to the nitrito species on the perovskite surfaces. Vibrational features at 1090 and 1194 cm^{-1} appearing only for low NO_2 (g) exposures and disappearing with increasing exposures are assigned to nitrite species. These FTIR assignments are also summarized in Table 6.

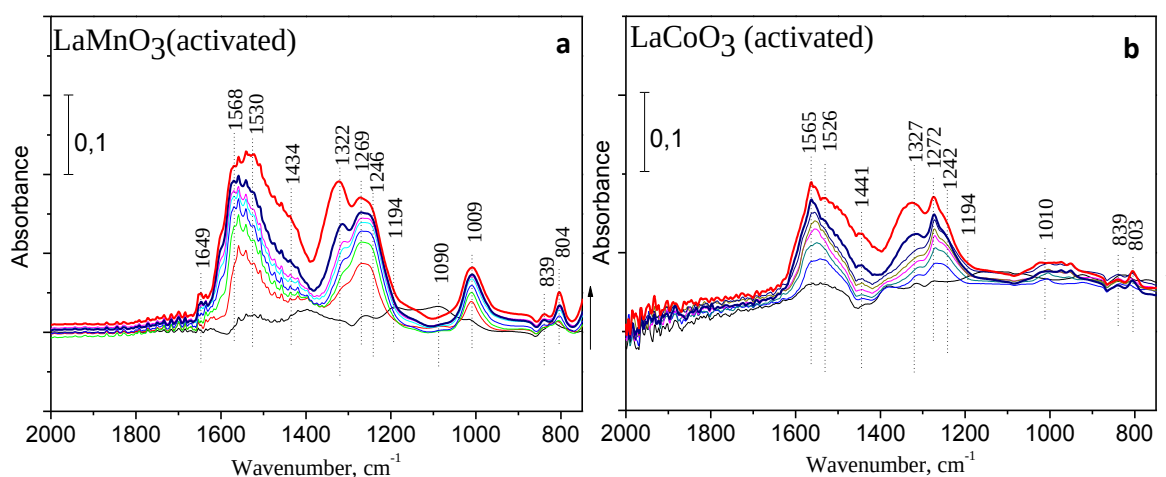


Figure 32. FTIR spectra of stepwise NO_2 (g) adsorption on activated a) LaMnO_3 and b) LaCoO_3 at 323 K.

Table 6. List of adsorbed species observed in this study with their corresponding characteristic IR vibrational [15-20]

<i>Vibrational Features Appearing Upon NO₂ Adsorption at 323 K</i>	<i>Adsorbed Species on LaMnO₃</i>
1530cm ⁻¹ , 1269cm ⁻¹	Monodentate Nitrate
1568cm ⁻¹ , 1246cm ⁻¹	Bidentate Nitrate
1649cm ⁻¹ , 1009cm ⁻¹ (v _s)	Bridging Nitrate
1434cm ⁻¹ (v _{N-O}), 1322cm ⁻¹ (v _{N-O})	Unidentate Nitrito
840-800cm ⁻¹ (v _{ONO,bending})	Unidentate Nitrito
1667cm ⁻¹	Carbonates
<i>Vibrational Features Appearing Upon NO₂ Adsorption at 323 K</i>	<i>Adsorbed Species on LaCoO₃</i>
1526cm ⁻¹ , 1272cm ⁻¹	Monodentate Nitrate
1565cm ⁻¹ , 1242cm ⁻¹	Bidentate Nitrate
1441cm ⁻¹ (v _{N-O}), 1320cm ⁻¹ (v _{N-O})	Unidentate Nitrito
840-800cm ⁻¹ (v _{ONO,bending})	Unidentate Nitrito
1897cm ⁻¹ (v _s) and 1818cm ⁻¹ (v _{as})	Co(II)-Dinitrosyl
1667cm ⁻¹	Carbonates

Most of the IR bands associated with NO₂ adsorption on the perovskite surfaces are very similar to those on pure La₂O₃ which is also given in Figure 33 as a control experiment. Thus, the surface adsorption properties of activated perovskites are close to those of La₂O₃. This is consistent with the previous Raman, SEM/EDX and XPS analysis suggesting that there exists some La-rich domains on the perovskite surfaces possibly due to the presence of La₂O₃.

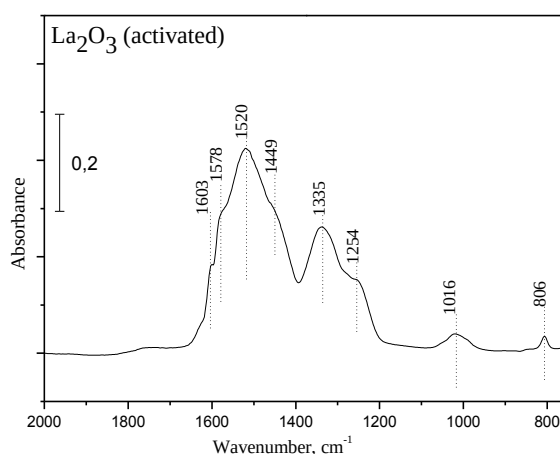


Figure 33. FTIR spectra of La₂O₃ saturated with 1.0 Torr of NO₂ (g) at 323 K.

The total amount of adsorbed NO_x species on the perovskite surfaces are different for LaMnO_3 and LaCoO_3 . Adsorption band intensities for LaMnO_3 (black spectrum) and LaCoO_3 (red spectrum) that were initially saturated with NO_2 (g) at 323 K are shown in Figure 34. According to the spectra, the NO_x uptake capacity of LaMnO_3 is higher than its Co-based counterpart which can be explained by the difference in the specific surface areas (SSA) of these perovskites. The SSA of LaMnO_3 is two times higher than that of LaCoO_3 .

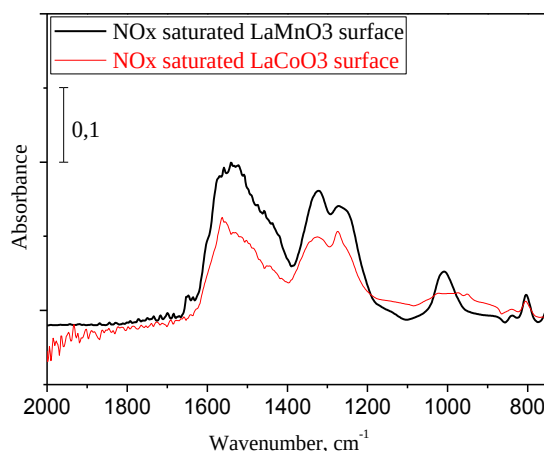


Figure 34. FTIR spectra of LaMnO_3 (black spectrum) and LaCoO_3 (red spectrum) surfaces saturated with 5.0 Torr NO_2 (g) at 323 K.

Thermal decomposition pathways of the adsorbed NO_x species were also investigated via FTIR spectroscopy as shown in Figure 35. NO_x saturated surfaces were thermally treated under vacuum in the temperature range of 323-823 K (Figure 35a and 35b). Investigation of the nitrate bands in the FTIR spectra reveals that nitrate decomposition on both perovskite surfaces is a gradual process without a sudden drastic attenuation of IR intensities. Nitrate bands disappear with relatively similar rates and the complete removal of the nitrate species occurs around 800 K.

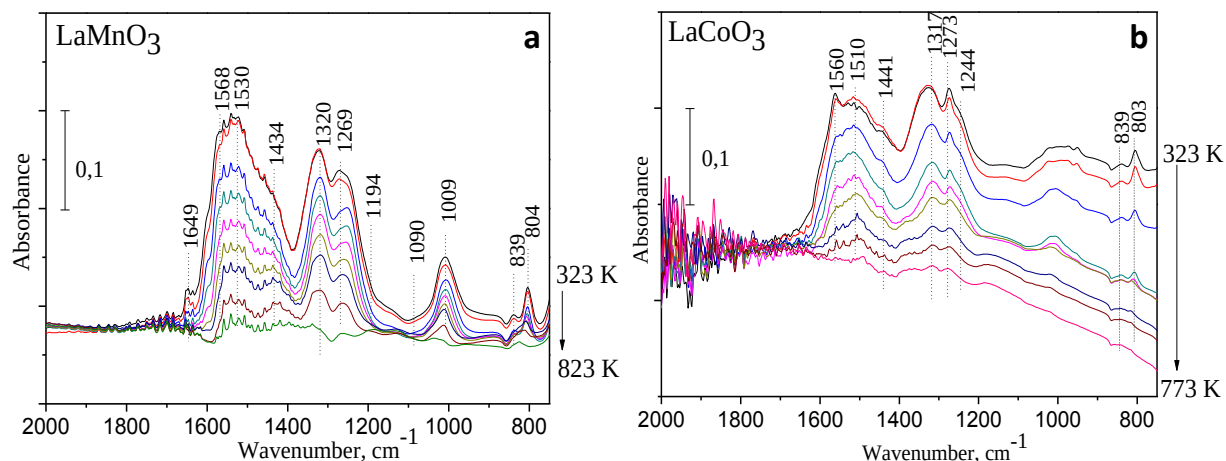


Figure 35. Temperature-dependent FTIR spectra for $\text{NO}_2(\text{g})$ saturated (a) LaMnO_3 and (b) LaCoO_3 samples between 323 K – 823 K.

In order to have a better understanding of the relative NO_x uptake capacities of LaMnO_3 and LaCoO_3 , TPD experiments were performed. Figure 36 shows NO_x desorption profiles from the activated perovskite surfaces. The major desorption channels are observed to be $m/z = 28, 30, 32, 44, 46$ corresponding to $\text{N}_2, \text{NO}, \text{O}_2, \text{N}_2\text{O}$ and NO_2 , respectively with the help of the TPD data, NSC of LaMnO_3 and LaCoO_3 can be compared. Such a comparison clearly indicates that LaMnO_3 has a higher NSC (by about 65% based on the integrated NO TPD signal (table 7)) than LaCoO_3 in excellent agreement with the current BET (Table 3) and in-situ FTIR (Figure 34) measurements. A detailed analysis of the desorbing species observed in the TPD data given in Figure 36 suggests that NO desorption occurs in a broad temperature window (i.e. 400-800 K) yielding multiple and convoluted desorption features and a global desorption maximum at c.a. 650 K. These convoluted NO desorption features can be better interpreted by analyzing the other simultaneously recorded desorption channels.

NO_2 ($m/z = 46$) desorption profiles given in Figures 36a corresponding to LaMnO_3 sample possess a line shape where at least two desorption states are discernible at c.a. 460 and 570 K. It is well-known that pure $\text{NO}_2(\text{g})$ can be readily fragmented inside a Quadrupole Mass Spectrometer (QMS) due to electron impact ionization yielding NO and NO_2 as the major signals, where NO: NO_2 ratio is found to be typically between

1:3 to 1:4. Thus, the characteristic NO desorption features in Figures 8a and 8b appearing at 460 and 570 K can be attributed predominantly to NO₂ desorption from the LaMnO₃ surface with some contribution from NO desorption. It is important to note that these desorption states do not reveal any simultaneous O₂(g) desorption signal. Temperature-programmed FTIR experiments (Figure 35a) performed in a parallel fashion to the current TPD experiments indicate that nitrates and nitrito species disappear in a gradual and a simultaneous manner during the heating ramp without a significant change in the line shape of the FTIR spectra. Thus, for the desorption window within 460-570 K, it can be argued that on the LaMnO₃ surface, nitrito and nitrate species desorb/decompose in the form of NO₂+NO (without O₂) where the O species generated during nitrate decomposition is captured by the perovskite curing oxygen-deficient point defects in the perovskite structure or in the case of Pd/LaMnO₃.

Another clearly visible signal appearing simultaneously with the NO and NO₂ desorption channels in the range of 490-570 K in Figures 36a is N₂O (m/z=44). N₂O desorption channel has a desorption maximum at c.a. 570 K which is coinciding with the high-temperature NO₂ desorption signal. Detection of N₂O is quite noteworthy as it indicates that even in the absence of an external reducing agent, LaMnO₃ surface can directly activate N-O linkages in a rather efficient manner and partially reduce nitrate (NO₃⁻) and nitrite (NO₂⁻) species above 500 K. As the N₂O formation implies the presence of atomic N species generated on the catalyst surface, recombinative desorption of atomic N in the form of N₂ as the direct total reduction product is also likely. As a matter of fact, m/z=28 desorption channel in Figures 36a clearly reveals the presence of N₂ desorption in a very broad temperature window with a local maximum at c.a. 570 K. Observation of N₂O and N₂ in the NO₂ TPD of LaMnO₃ clearly shows that these surfaces can be promising materials as DeNO_x catalysts, as they can directly reduce stored NO_x species (i.e nitrates and nitrites) even in the absence of an external reducing agent.

At higher temperatures, an additional TPD feature in the m/z=32 channel becomes apparent in Figures 36a. This strong O₂ desorption signal located within 750-800 K is detected together with an intense NO desorption signal appearing at the same temperature. In other words, in this temperature interval, NO_x species remaining on

the surface decompose as $\text{NO} + \text{O}_2$ with a less significant contribution from N_2 and N_2O (note that NO_2 desorption is not detected at this temperature). Temperature-programmed FTIR studies (Figure 35a) suggest that at this temperature nitrito species are the prominently existing NO_x species on LaMnO_3 with a smaller contribution from nitrates. Thus, it is apparent that these thermally stable bridging nitrites decompose mostly in the form of $\text{NO} + \text{O}_2$. It is worth mentioning that the high temperature O_2 desorption feature appearing within 750-800 K can also be associated to the direct oxygen evolution from LaMnO_3 and the formation of oxygen vacancies in the perovskite structure [106].

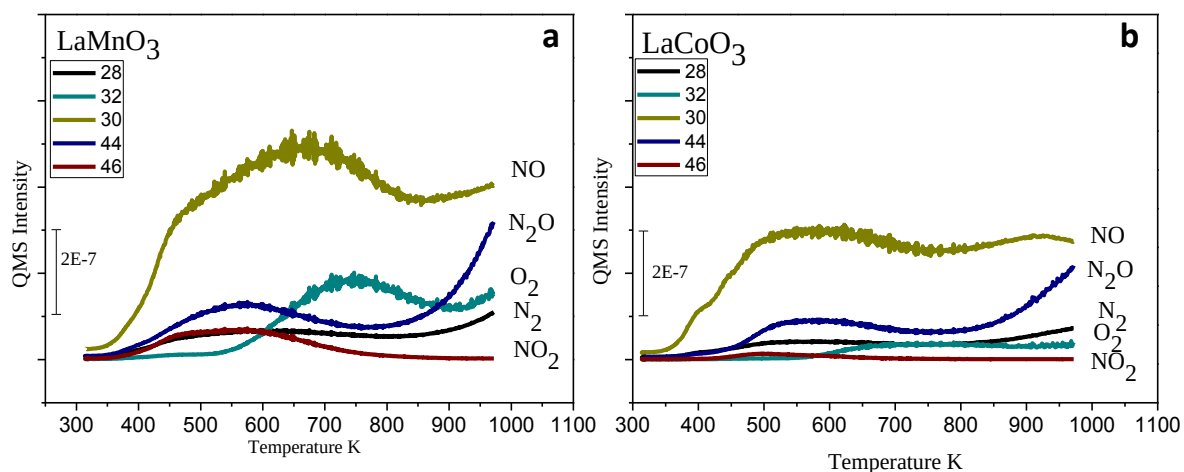


Figure 36. TPD profiles obtained after $\text{NO}_2(\text{g})$ saturation at 323 K of activated (a) LaMnO_3 and (b) LaCoO_3 .

Table 7. Integrated areas under NO (30 amu) desorption curve.

Sample Name	Integrated area under NO curve
Activated- LaMnO_3	2.32 E-4
Activated- LaCoO_3	1.53 E-4

4.2.1.2. NO_x Adsorption and Desorption Behavior of Reduced Perovskite Surfaces

Before the NO_x adsorption experiments, the perovskite surfaces were pre-treated with an aggressive reducing agent, H_2 , which causes significant structural changes on

perovskite structures [21, 22]. The effect of H₂ (g) pretreatment on NO_x adsorption profiles for both LaMnO₃ (Figure 37a) and LaCoO₃ (Figure 37b) are shown in Figure 37. The resulting FTIR spectra show that the extent of NO_x adsorption for both materials drastically increases after the initial reduction of the surfaces with H₂ (g) (5.0 Torr H₂ (g) at 623 K for 10 min). Destruction and re-construction of the perovskite structure upon reduction under severe conditions is widely studied in literature [11, 21-24]. The alterations of the structure are possibly associated with the reduction of the B site cations (i.e. reduction of Mn(III) and Co(III) into Mn^{3+(-x)} and Co^{3+(-x)}) when the sample is exposed to extreme reducing conditions. Dacquin et al. showed the destruction of perovskite structure into Co⁰/CoO_x/La₂O₃ via in-situ XRD and XPS upon H₂ pre-treatment [11, 23]. A similar conclusion can be deduced for the LaMnO₃ sample, which may involve a transformation of the perovskite structure into a Mn⁰/MnO/La₂O₃ system although the reduction is not as significant as its Co-based counterpart. The reduction of Mn(III) and Co(III) can be also observed by examining the NO₂(g) adsorption on the reduced LaMnO₃ and LaCoO₃ surfaces. In Figure 37b, IR band frequencies at 1897 cm⁻¹ (ν_s) and 1818 cm⁻¹ (ν_{as}) correspond to N-O stretching modes of surface dinitrosyl species on Co²⁺ [25-27]. Further evidence for alteration in the electronic structure for Co-based perovskite structure is the tilt in the baseline of the spectra as shown in Figure 37b. Moreover, dinitrosyl species on Mn⁺² appeared at 1771 cm⁻¹ in Figure 37a (inset) [28] but these species are not as pronounced as for the Co-based perovskite. It is obvious that the surface coordination characteristics of adsorbed NO_x species were transformed from nitrate into nitrite/nitrito/nitro/hyponitrite upon H₂ pretreatment where the vibrational frequencies (1487, ~1450 and 1330 cm⁻¹) related to nitrite/nitrito/nitro features become dominant over all other nitrate-related (1567 and 1270cm⁻¹) vibrations [10,26]. For both Mn and Co-based perovskites, surface nitrate/nitrite species are similar even after reduction which is in line with the fact that NO_x species are adsorbed on La-related sites after the reduction process.

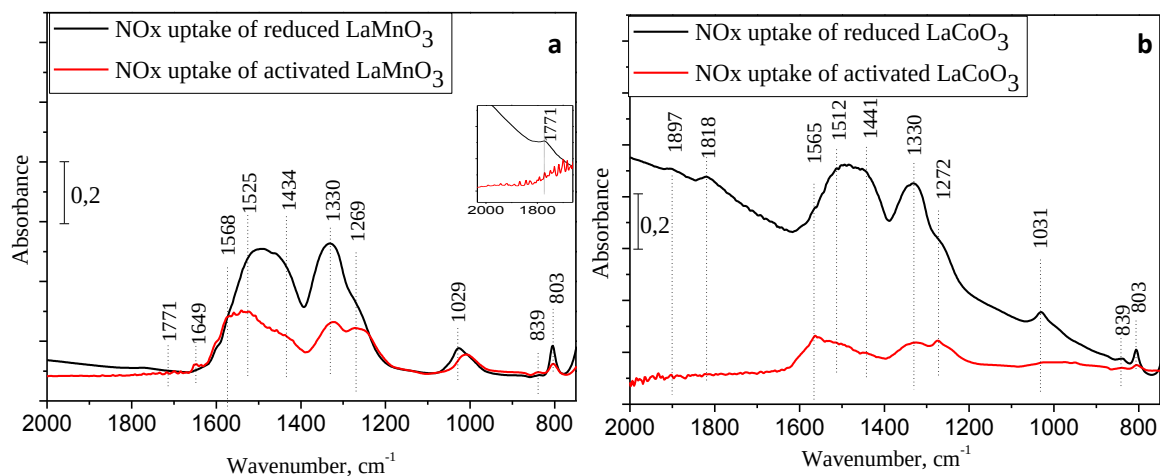


Figure 37. FTIR spectra of saturated surfaces with 5.0 Torr $\text{NO}_2(\text{g})$ at 323 K. a) reduced LaMnO_3 (black spectrum) and LaMnO_3 (red spectrum), b) reduced LaCoO_3 (black spectrum) and LaMnO_3 (red spectrum).

The next set of TPD experiments was performed on $\text{H}_2(\text{g})$ pre-treated perovskite surfaces in order to support the FTIR data analysis discussed above. Figures 38 and 39 demonstrate the NO_x desorption profiles of the fresh/activated (a) and reduced (b) surfaces of LaMnO_3 and LaCoO_3 , respectively. Rather than a slow and a gradual NO_x desorption, the reduced samples demonstrate a much more abrupt NO_x release behavior appearing at lower temperatures (i.e. 480 K and 420 K for LaMnO_3 and LaCoO_3 , respectively). More interestingly, the TPD profiles of activated LaCoO_3 (Figure 39a) and reduced LaCoO_3 (Figure 39b) are completely different. The difference is due to the complete reduction of the perovskite structure into $\text{Co}^0/\text{CoO}_x/\text{La}_2\text{O}_3$. The TPD profile of activated LaCoO_3 shows a gradual desorption profile whereas sharp desorption of NO at 420 K was observed on reduced LaCoO_3 . These intense low-temperature desorption signals can also be associated with the desorption/decomposition of weakly bound dinitrosyl species (illustrated in the FTIR results given in Figure 37) which are formed on the reduced $\text{Co}^0/\text{Co}^{2+}$ species. However it is worth emphasizing that due to the relatively low desorption temperature of all of the NO_x species, pre-reduced LaCoO_3 sample does not seem to possess a significant high-temperature NO_x storage capacity. Moreover, direct decomposition of NO to N_2 is observed after reduction of LaCoO_3 (Figure 39b). For both of the reduced perovskite surfaces, integrated areas under the NO (30 amu)

desorption curves are obviously higher than those of the fresh surfaces as shown in Table 8. This clearly indicates that the NO_x uptake capacities of H₂(g)-treated and reduced perovskite surfaces are relatively higher than that of the freshly activated surfaces. This might also be associated with the formation of La₂O₃ phase after reduction of perovskite because La₂O₃ can act as a NO_x storage material [80].

Table 8. Integrated areas under NO (30 amu) desorption curve.

Sample Name	Integrated area under NO curve
Activated-LaMnO ₃	2.32 E-4
Reduced-LaMnO ₃	3.72 E-4
Activated-LaCoO ₃	1.53 E-4
Reduced-LaCoO ₃	2.91 E-4

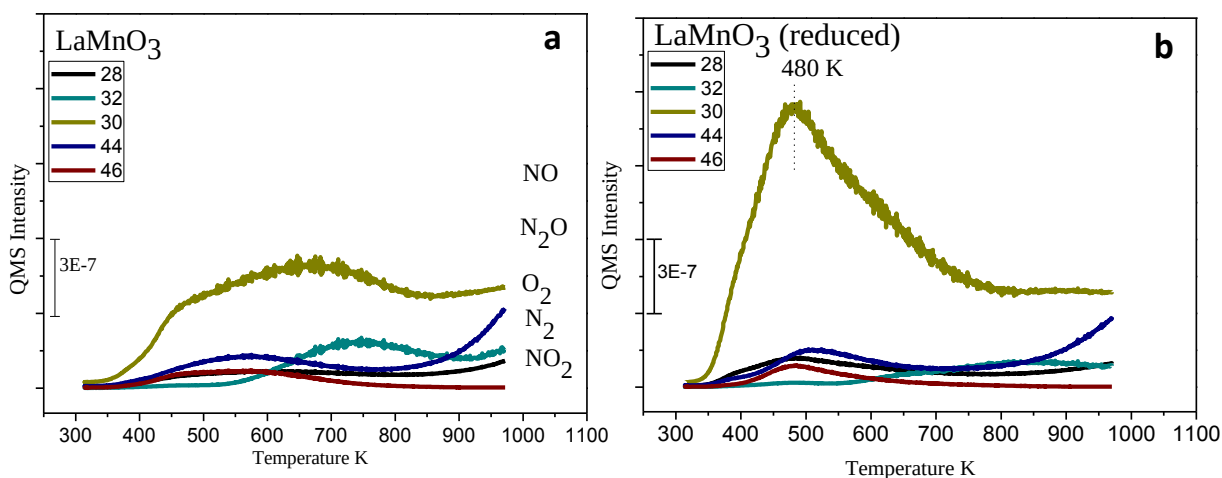


Figure 38. TPD profiles obtained after NO₂(g) saturation at 323 K of (a) LaMnO₃ and (b) reduced LaMnO₃.

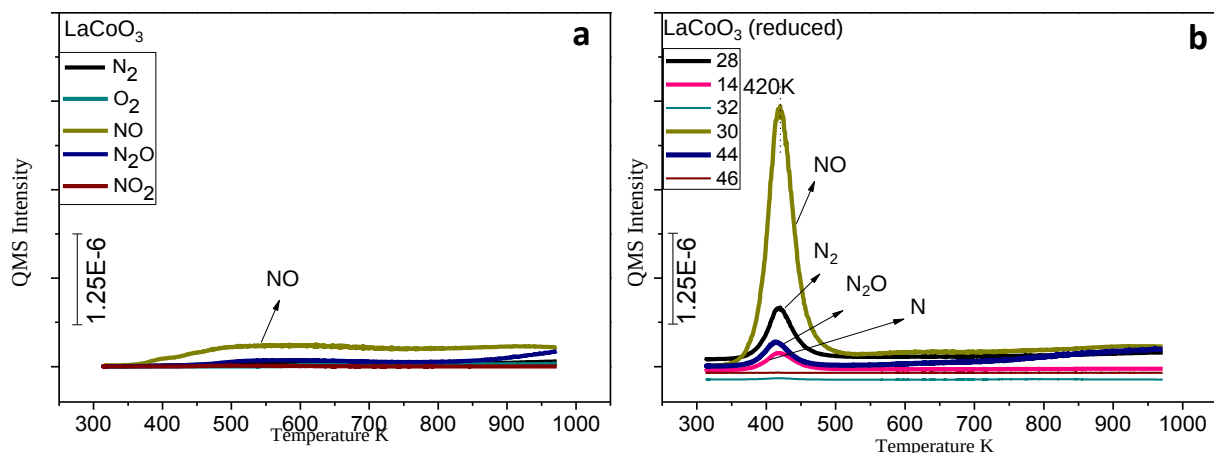


Figure 39. TPD profiles obtained after $\text{NO}_2(\text{g})$ saturation at 323 K of (a) fresh LaCoO_3 and (b) reduced LaCoO_3 .

4.2.1.3. Effect of Palladium on NO_x Adsorption and Desorption Behavior

Figure 40 shows the FTIR spectra of LaMnO_3 and Pd/LaMnO_3 samples, illustrating the influence of Pd incorporation on the NO_x adsorption behavior of Mn-based perovskite surfaces. NO_x adsorption on the perovskite surfaces was performed via multiple ($0.1 \text{ Torr} \times 1 \text{ min}$) NO_2 exposures with a final saturating exposure ($5.0 \text{ Torr} \times 10 \text{ min NO}_2$) at 323 K (Figures 40 and 41). Palladium incorporation does not lead to a drastic alteration in the NO_x adsorption profiles, meaning that both samples share similar adsorption geometry and vibrational frequencies of NO_x species. However a minor difference resulting from Pd incorporation can still be detected for Mn-containing perovskites (Figure 40). The intensities of all the vibrational bands in the FTIR spectra monitored after NO_x uptake are slightly suppressed for the Pd/LaMnO_3 sample surface (Figure 40b). Furthermore, the relative intensities of the 1322, 1269 and 1246 cm^{-1} bands also slightly change (Figure 40a and 40b). The 1322 cm^{-1} band corresponds to monodentate nitrite surface species ($\nu_{\text{N-O}}$), while the 1269 and 1246 cm^{-1} bands correspond to monodentate and bidentate nitrate species, respectively [15-20]. The attenuation of the nitrite bands and the corresponding increase in the intensities of the nitrate-related bands for the palladium-containing perovskite illustrates the enhancement in the catalytic oxidation of nitrites into nitrates via Pd sites. The FTIR spectra presented in Figure 41 demonstrate the NO_x

adsorption behavior on LaCoO_3 and Pd/LaCoO_3 . Pd incorporation into the Co-based perovskite structure has almost no effect on NO_x adsorption profiles. For the Co-containing samples (Figure 41), overall IR intensities do not tend to decrease as compared to those of LaMnO_3 and Pd/LaMnO_3 (Figure 40).

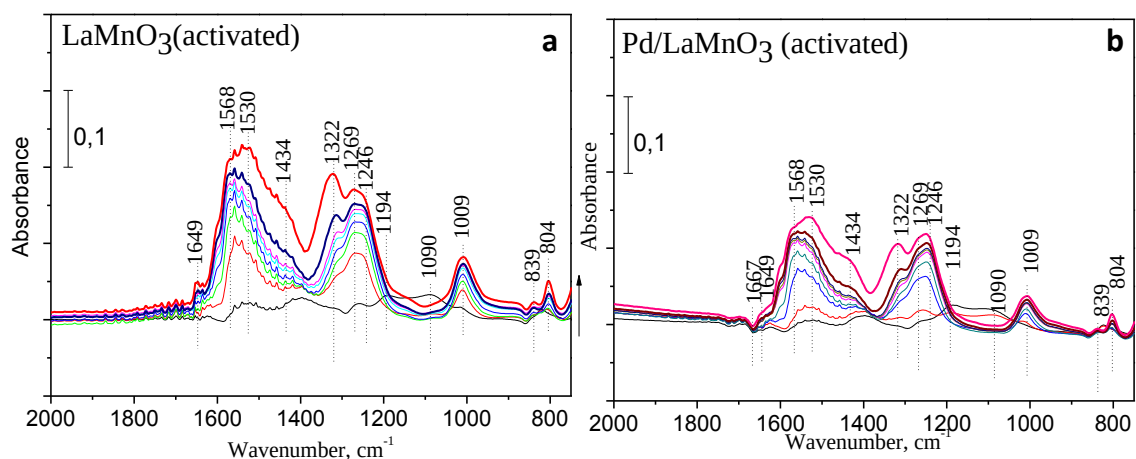


Figure 40. FTIR spectra for stepwise $\text{NO}_2(\text{g})$ adsorption on activated a) LaMnO_3 and b) Pd/LaMnO_3 at 323 K

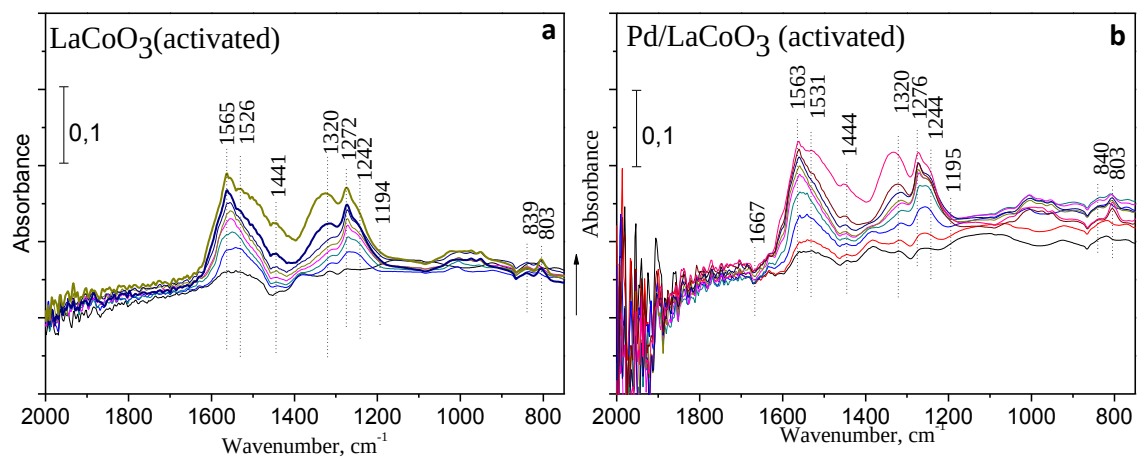


Figure 41. FTIR spectra for stepwise $\text{NO}_2(\text{g})$ adsorption on activated a) LaCoO_3 and b) Pd/LaCoO_3 at 323 K

Thermal decomposition of the adsorbed NO_x species on the synthesized perovskite catalysts was also investigated via FTIR spectroscopy (Figures 42, Figure 43). The

FTIR spectra corresponding to the stepwise heating of the nitrated LaMnO_3 and Pd/LaMnO_3 samples are presented in Figure 42. NO_x saturated surfaces were thermally treated under vacuum in the temperature range of 323–823 K. It is apparent that upon thermal annealing, all of the vibrational band intensities diminish simultaneously without any significant change in the spectral line shapes. This observation indicates that the nature of the adsorbed NO_x species do not significantly change upon annealing, while their surface coverages monotonically decrease due to decomposition/desorption phenomena. Although, the thermal stabilities of NO_x species adsorbed on LaMnO_3 and Pd/LaMnO_3 surfaces seem to be somewhat similar, some differences can still be recognized. Figure 42 suggests that almost all of the NO_x related bands disappear around 800 K for the LaMnO_3 (Figure 42a) sample. However, for Pd/LaMnO_3 (Figure 42b) this temperature is lower, i.e. 700 K. Thus, Pd incorporation seems to decrease the nitrate/nitrite decomposition temperature to a certain extent. It is worth mentioning that such a destabilization of the adsorbed NO_x species is not visible for the Co-containing perovskite samples (Figure 43) where nitrate bands disappear above 773 K for both LaCoO_3 (Figure 43a) and Pd/LaCoO_3 (Figure 43b) samples.

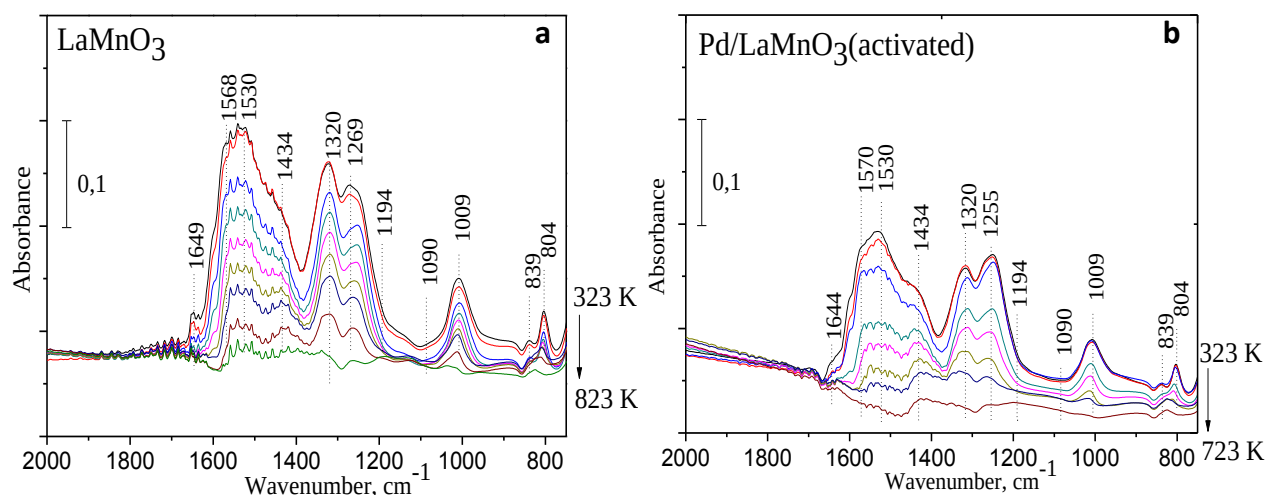


Figure 42. Temperature-dependent FTIR spectra for $\text{NO}_2(\text{g})$ saturated (a) LaMnO_3 and (b) Pd/LaMnO_3 samples between 323 K – 823 K.

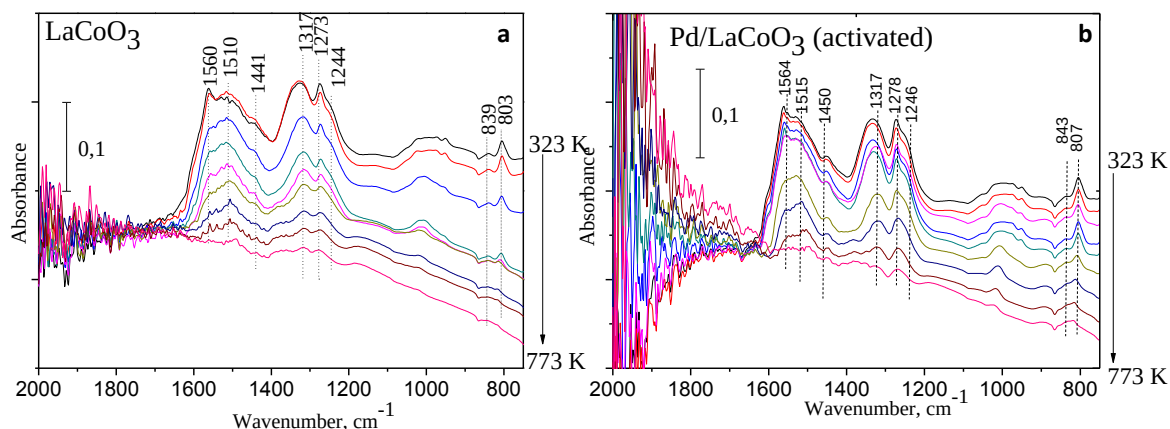


Figure 43. Temperature-dependent FTIR spectra for $\text{NO}_2(\text{g})$ saturated (a) LaCoO_3 and (b) Pd/LaCoO_3 samples between 323 K – 823 K.

To support the FTIR results that were mentioned above, TPD experiments were performed on activated Pd/perovskite samples. TPD profiles of the activated perovskites are shown in Figure 44 with the major desorption channels of 30, 32 and 44 amu, corresponding to NO , O_2 and $\text{N}_2\text{O}/\text{CO}_2$. For the LaMnO_3 (Figure 44a) and Pd/LaMnO_3 (Figure 44b) samples, the NO desorption channel is quite similar and has a major broad desorption signal with a maximum around 600-700 K revealing a shoulder at around 400-500 K. The TPD results presented in Figures 42a and 42b suggest that Pd incorporation does not seem to have a very significant influence either on the total NO_x storage capacity or on the relative thermal stability of the adsorbed NO_x species. This is in relatively good agreement with the FTIR data presented in Figure 42, as well as the corresponding SSA values of the activated LaMnO_3 and Pd/LaMnO_3 catalysts. On the other hand, as expected from the FTIR data given in Figure 34, the NO desorption signal is weaker for the LaCoO_3 sample (Figure 44c) with respect to that of the LaMnO_3 sample (Figure 44a) and reveals a broader line shape with a poorly resolved maximum in the 500-650 K range and a shoulder at c.a. 400 K. For the Pd/LaCoO_3 (Figure 44d) sample, the main broad desorption feature is shifted to 650-850 K, while the low temperature desorption feature appearing at 430 K is significantly sharpened. Pd addition also increases the thermal stability of the stored NO_x species shifting their desorption signals to higher temperatures. In particular, Figure 44d also illustrates that Pd addition leads to a sharp low-temperature NO desorption signal located at 430 K. Corresponding

temperature-dependent FTIR data indicate that, at these temperatures monodentate and bridging nitrates are partially destroyed. It is also worth emphasizing that this enhanced low-temperature NO desorption signal is concomitant to N₂O and N₂ signals appearing at the same temperature. Thus, it is clear that Pd incorporation has a minor but detectable positive influence on the low-temperature direct total/partial NO_x reduction on the Co-based perovskite systems. The data from TPD experiments given in Figures 44 indicate that Pd incorporation into the perovskite structure enhances the NO_x storage capacity (NSC) as seen in Table 9. Since the Pd/La ratio determined via XPS is higher for Pd/LaCoO₃ than Pd/LaMnO₃, suggesting a better Pd dispersion, the higher enhancement of NSC for Pd/LaCoO₃ is expected.

Table 9. Integrated areas under NO (30 amu) desorption curve for activated Pd-free and Pd/perovskites.

Sample Name	Integrated area under NO curve
Activated-LaMnO ₃	2.32 E-4
Activated-Pd/LaMnO ₃	2.51 E-4
Activated-LaCoO ₃	1.53 E-4
Activated-Pd/LaCoO ₃	1.91 E-4

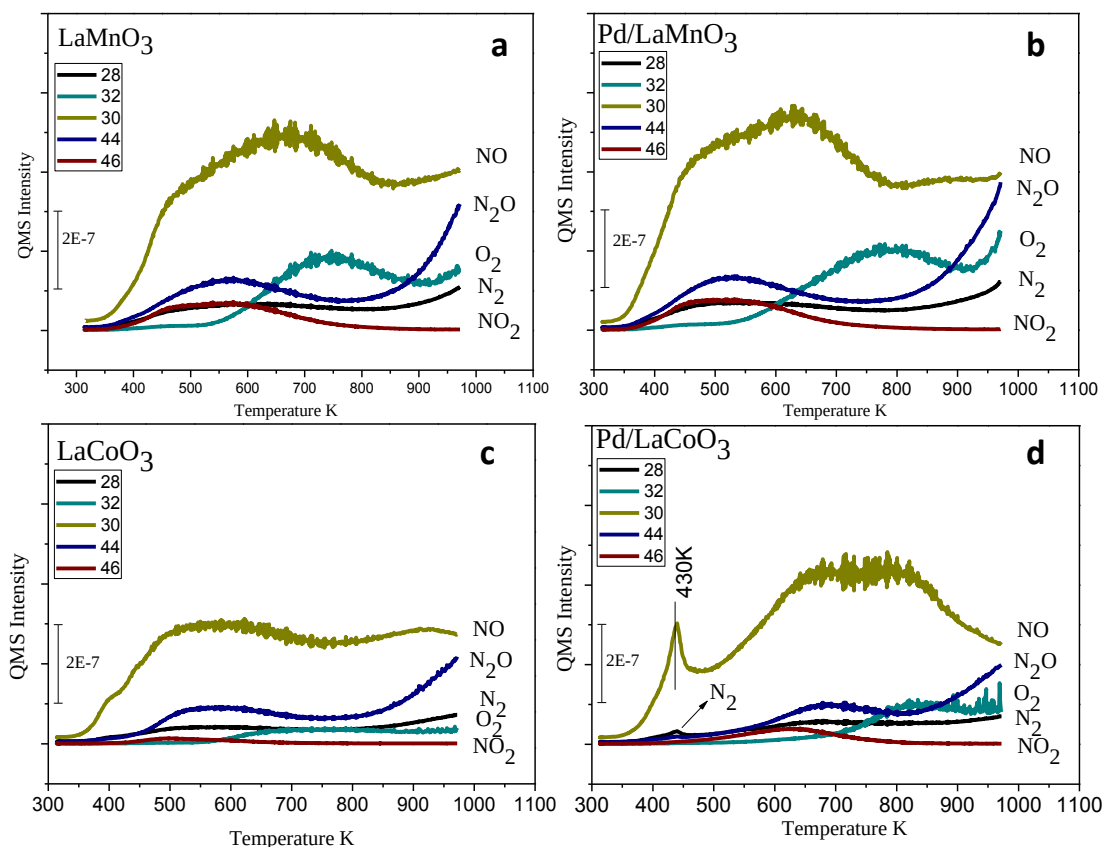


Figure 44. TPD profiles obtained after $\text{NO}_2(\text{g})$ saturation at 323 K of activated (a) LaMnO_3 , (b) Pd/LaMnO_3 , (c) LaCoO_3 , (d) Pd/LaCoO_3 .

4.2.1.4. NO_x Adsorption and Desorption Behavior of Reduced Pd/Perovskite Surfaces

The effect of $\text{H}_2(\text{g})$ pre-treatment on the NO_x uptake profiles of Pd-containing and Pd-free perovskites is illustrated in Figure 45. Prior to this set of experiments, the perovskite surfaces were reduced in 5 Torr $\text{H}_2(\text{g})$ at 623 K for 10 min inside the FTIR cell. The changes in the NO_x adsorption profiles for LaMnO_3 and LaCoO_3 can be attributed to the partial reduction of the B-site cations (Mn or Co). Pd incorporation does not have a significant effect on adsorbed NO_x species even after reduction of the surfaces. Detailed spectral assignments of the corresponding FTIR bands for the NO_x adsorption on reduced perovskite samples were provided in the section 4.2.1.1 and 4.2.1.2. Figures 45a and 45b show the FTIR spectra corresponding to the NO_x -saturated (via 5.0 Torr $\text{NO}_2(\text{g})$ exposure at 323 K) activated/reduced LaMnO_3 and Pd/LaMnO_3 samples, respectively. In a similar

fashion, the spectra related to the Co-containing materials are presented in Figures 45c and 45d. The red spectra in each panel represent the activated perovskite surfaces whereas the black spectra correspond to the reduced surfaces (Figure 45). It is apparent in Figure 45 that initial reduction of all of the perovskite surfaces with/without Pd via H_2 leads to a drastic increase in the NO_x uptake. Furthermore, this effect is significantly more pronounced for the Pd/LaMnO₃ and Pd/LaCoO₃ samples. It is clear that the initial reduction with H_2 (g) leads to a significant boost in the NO_x storage capacity of all of the samples. This effect is particularly noticeable for the Pd/LaCoO₃ sample since the dispersion of palladium on Pd/LaCoO₃ is higher than that of Pd/LaMnO₃ as shown in Table 4. These experiments clearly demonstrate the delicate surface properties of the Pd-containing perovskite catalysts and the significant changes in their NO_x storage capacities that can readily be tailored by proper catalyst pre-treatment. Such pre-treatment strategies can be exploited to design new catalyst formulations with improved NO_x storage capacities.

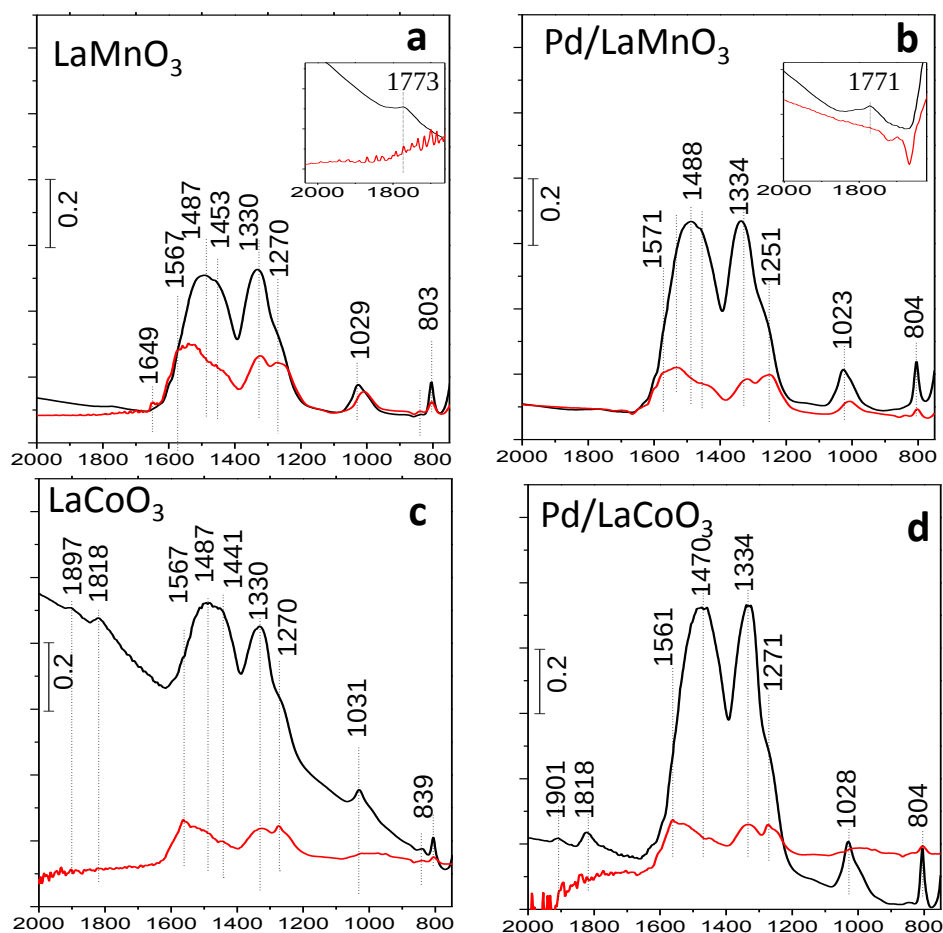


Figure 45. FTIR spectra of surfaces saturated with 5.0 Torr NO₂(g) at 323 K. a) reduced LaMnO₃ (black spectrum) and LaMnO₃ (red spectrum), b) reduced Pd/LaMnO₃ (black spectrum) and LaMnO₃ (red spectrum), c) reduced LaCoO₃ (black spectrum) and LaCoO₃ (red spectrum), d) reduced Pd/LaCoO₃ (black spectrum) and Pd/LaCoO₃ (red spectrum).

The NO_x desorption TPD profiles of H₂ (g) pretreated perovskites are presented in Figure 46. A quick glance at the scale bars of the TPD signals given in Figure 46 in comparison to that of Figure 44 (TPD profiles of activated samples) immediately points to the fact that H₂ (g) pretreatment significantly increases the total NO_x uptake for all samples. For the Mn- containing samples (Figure 46a and 46b) a major and an asymmetrical NO desorption signal is observed with a temperature maximum located

at 480-510 K. It is important to note that the desorption signal line shapes of the activated (Figure 44a and 44b) and reduced (Figure 46a and 46b) LaMnO_3 and Pd/LaMnO_3 samples are rather similar indicating that the thermal stability of the adsorbed species do not change upon initial reduction of the LaMnO_3 and Pd/LaMnO_3 surfaces. These observations are in line with the higher structural integrity of the Mn-containing samples which can be preserved even after moderate reduction conditions. Similar experiments performed on Co-containing samples (Figures 46c and 46d) reveal a clear contrast to the previously mentioned findings on Mn-based perovskites. Figure 46c indicates that the TPD profiles of the reduced LaCoO_3 perovskites are significantly modified with respect to that of their activated counterparts, demonstrating a sharp NO (and accompanying N_2 and $\text{N}_2\text{O}/\text{CO}_2$) desorption signal at 420 K without an intense high-temperature desorption tail. Apparently, the reduction procedure significantly modifies the Co-containing perovskite structure and decreases the thermal stabilities of the stored nitrate/nitrite species. On the other hand, Pd incorporation to the LaCoO_3 perovskite structure (Figure 46d) leads to a desorption profile which resembles that of the activated samples. For the reduced Pd/LaCoO_3 catalysts (Figure 46d), the major NO desorption signal peak is located at 580 K, demonstrating that the presence of Pd stabilizes the adsorbed nitrite/nitrate states. Through Pd addition and H_2 -pretreatment (Figure 46d), pre-reduced Pd/LaCoO_3 system gains both low-temperature (i.e. 430 K) as well as high-temperature (i.e. 580 K) NO_x storage capabilities without compromising its ability towards direct NO_x reduction and $\text{N}_2/\text{N}_2\text{O}$ production. As a matter of fact, comparison of Figures 46c and 46d immediately reveals that the amount of $\text{N}_2/\text{N}_2\text{O}$ generated via direct NO_x reduction is significantly enhanced upon Pd addition and pre-reduction. It is apparent that Pd incorporation on the LaCoO_3 surface strengthens the structural integrity towards reduction without compromising the NO_x storage capacity. In the literature, it is well known that the presence of a noble metal decreases the reduction temperature of Co-based perovskites [23, 29-32]. Pd/perovskite preserves the structural integrity as seen in the TPD profiles given in Figure 46, possibly because Pd prevents the growth of metallic Co particles [29]. It is also important to note that for the reduced LaCoO_3 and Pd/LaCoO_3 samples (Figures 46c and 46d) direct nitrate reduction to N_2 can also be observed which is not visible for the Mn-containing samples (Figures 46a and 46b).

Table 10. Integrated areas under NO (30 amu) desorption curve for reduced Pd-free and Pd/perovskites.

Sample Name	Integrated area under NO curve
Reduced-LaMnO ₃	3.72 E-4
Reduced-Pd/LaMnO ₃	5.31 E-4
Reduced-LaCoO ₃	2.91 E-4
Reduced-Pd/LaCoO ₃	4.10 E-4

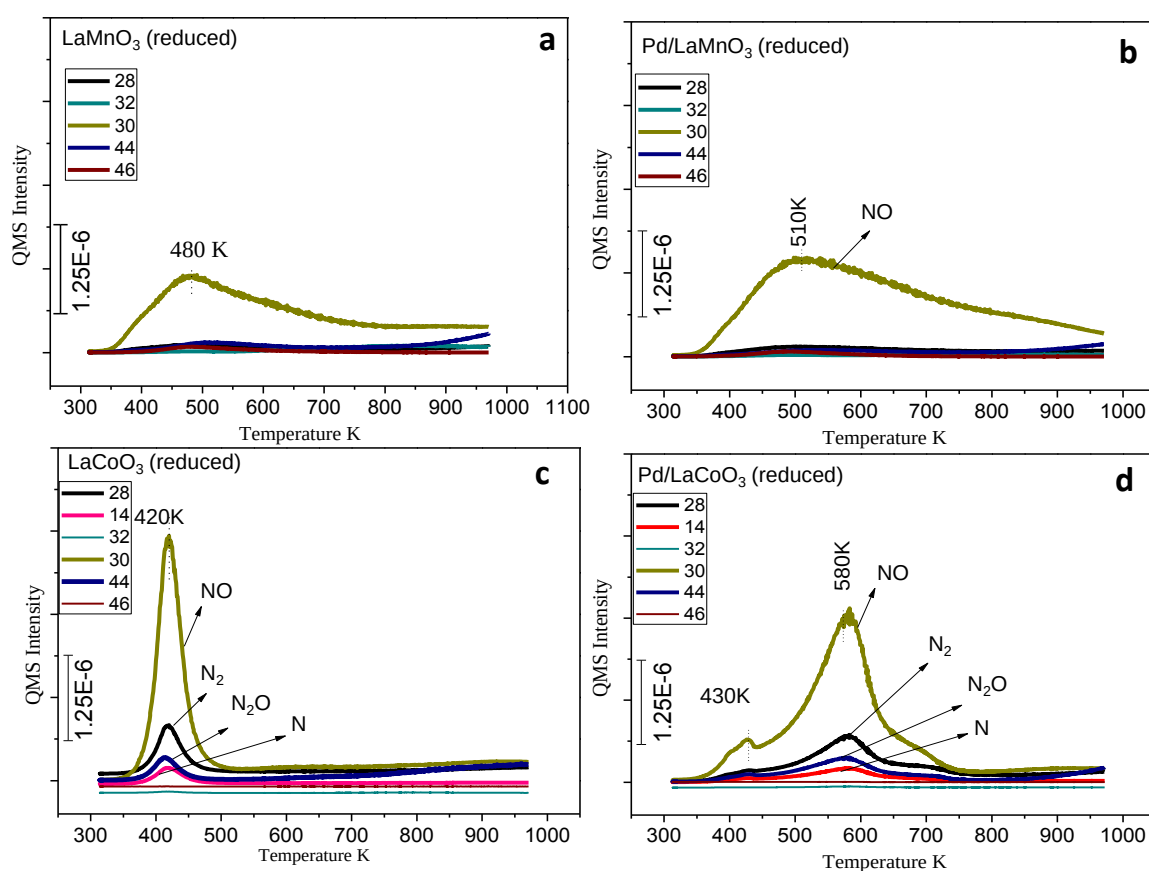


Figure 46. TPD profiles obtained after NO₂(g) saturation at 323 K of reduced (a) LaMnO₃, (b) Pd/LaMnO₃, (c) LaCoO₃, (d) Pd/LaCoO₃.

4.3. FTIR Spectroscopic Analysis of SO_x Uptake of the Synthesized Materials

4.3.1. Sulfation and De-sulfation Behavior of Perovskites

SO_x uptake capacity was investigated for LaMnO₃ and LaCoO₃ perovskite materials via in-situ FTIR as shown in Figure 47. The bottom set of FTIR spectra in each panel

of Figure 47 were recorded at 323 K after the samples were exposed to 2.0 Torr of SO_2+O_2 gas mixture ($\text{SO}_2:\text{O}_2 = 1:10$) at 323 K, 373 K, 473 K and 673 K for 15 min. Next, the SO_2+O_2 gas mixture was evacuated and the upper sets of spectra were obtained after the samples were annealed in vacuum at 473, 673, 873 and 1073 K for 15 min. The spectra in Figure 43 reveal four main features at around 1240, 1137, 1058 and 986 cm^{-1} . The peak at 1058 and 986 cm^{-1} can be attributed bidentate sulfates, whereas, bulk-like sulfates appeared at 1240 and 1137 cm^{-1} [33-35]. A minor feature at 1396 cm^{-1} , which was assigned to sulfite-like species, is also present in Figure 47 [35]. With the intensities of the spectra shown in Figure 47, one can infer that LaMnO_3 (Figure 47a) has a higher tendency towards sulfur accumulation as compared to LaCoO_3 (Figure 47a) this can be explained by the higher surface basicity of manganese with respect to cobalt [103]. For both LaCoO_3 and LaMnO_3 , sulfur species are stable up to 873 K during heating in vacuum and bulk sulfates are formed at 1073 K as seen in the upper set of spectra in Figure 47.

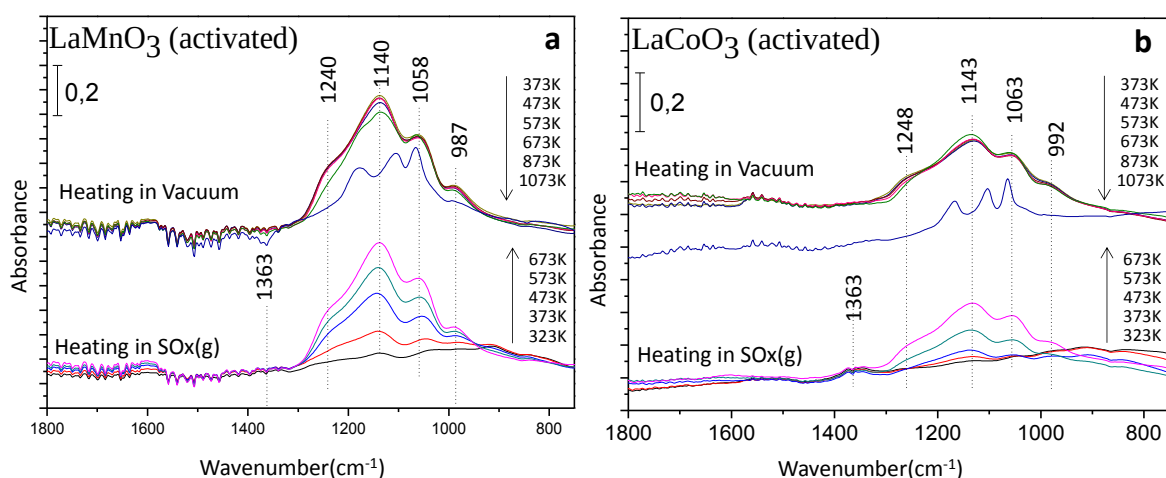


Figure 47. FTIR spectra related to SO_x uptake and release properties of a) LaMnO_3 , and c) LaCoO_3 . Bottom set of spectra in each panel were acquired after SO_x exposure (2.0 Torr, $\text{SO}_2:\text{O}_2 = 1:10$) at 323 K, followed by annealing at 373, 473 and 673K in the SO_x gas mixture for 15 min. Upper set of spectra in each panel were acquired by heating at 473, 673, 873 and 1073 K for 15 min under vacuum and after SO_x gas mixture is evacuated. All spectra were acquired at 323 K in vacuum

4.3.2. Effect of Palladium on SO_x Adsorption and Desorption Behavior of Perovskites

The effect of Pd incorporation on the SO_x uptake capacity was investigated for perovskite materials via in-situ FTIR as shown in Figure 48. Pd incorporation seems to have no significant effect on the type of adsorbed SO_x species on LaMnO₃ (Figure 48a), Pd/LaMnO₃ (Figure 48b), LaCoO₃ (Figure 48c) and Pd/LaCoO₃ (Figure 48d). After the sulfation of perovskite samples indicated at the bottom in Figure 48, it is clearly seen that the SO_x absorption intensities of Pd/LaMnO₃ (Figure 48b) and Pd/LaCoO₃ are three times higher than those of LaMnO₃ (Figure 48a) and LaCoO₃ (Figure 48c), respectively. This indicates that presence of palladium leads to a strong increase in the SO_x uptake during the sulfation process. It is likely that Pd sites catalyze the SO₂ oxidation and sulfite/sulfate accumulation on the catalyst surfaces. After the sulfation process, thermal regeneration of sulfur species was investigated as shown in the top spectra in Figure 44. It is clearly seen that Pd has no crucial role for desorption of surface SO_x between 373-673 K since all of the sulfite/sulfate bands still appear at the same positions. However, at 873 K, the peak at 1250 cm⁻¹ which was attributed to the bulk-like sulfate [33-35] as described in the previous section disappears for Pd/LaMnO₃ (Figure 48b) whereas it remains for LaMnO₃ (Figure 48a) although its intensity slightly decreases. After annealing the Mn-based perovskites at 1073 K, the intensity and the position of the remaining sulfur signals are approximately similar although Pd/LaMnO₃ stores three times more SO_x than LaMnO₃ during the sulfation process. It was concluded that despite higher SO_x storage capacity of Pd/LaMnO₃ compared to the Pd-free counterpart, it releases most of the stored SO_x reversibly during the thermal regeneration process. The minor remaining sulfur species for both LaMnO₃ and Pd/LaMnO₃ are bulk sulfates. For the LaCoO₃ and Pd/LaCoO₃ samples (Figure 48c and Figure 48d), removal of surface sulfate/sulfite species was not observed during heating between 373-873 K like Mn-based perovskites (Figure 48a and Figure 48b). However, while annealing in vacuum at 1073 K, the Co-based perovskite samples reveal a starkly distinct behavior compared to their Mn-based counterparts. Sulfur poisoning is rather irreversible on both LaCoO₃ and Pd/LaCoO₃ with the formation of bulk sulfates at 1073 K. Thermal regeneration of surface sulfur in vacuum is not possible by annealing at temperatures less than or equal to 1073 K for Co-based perovskites.

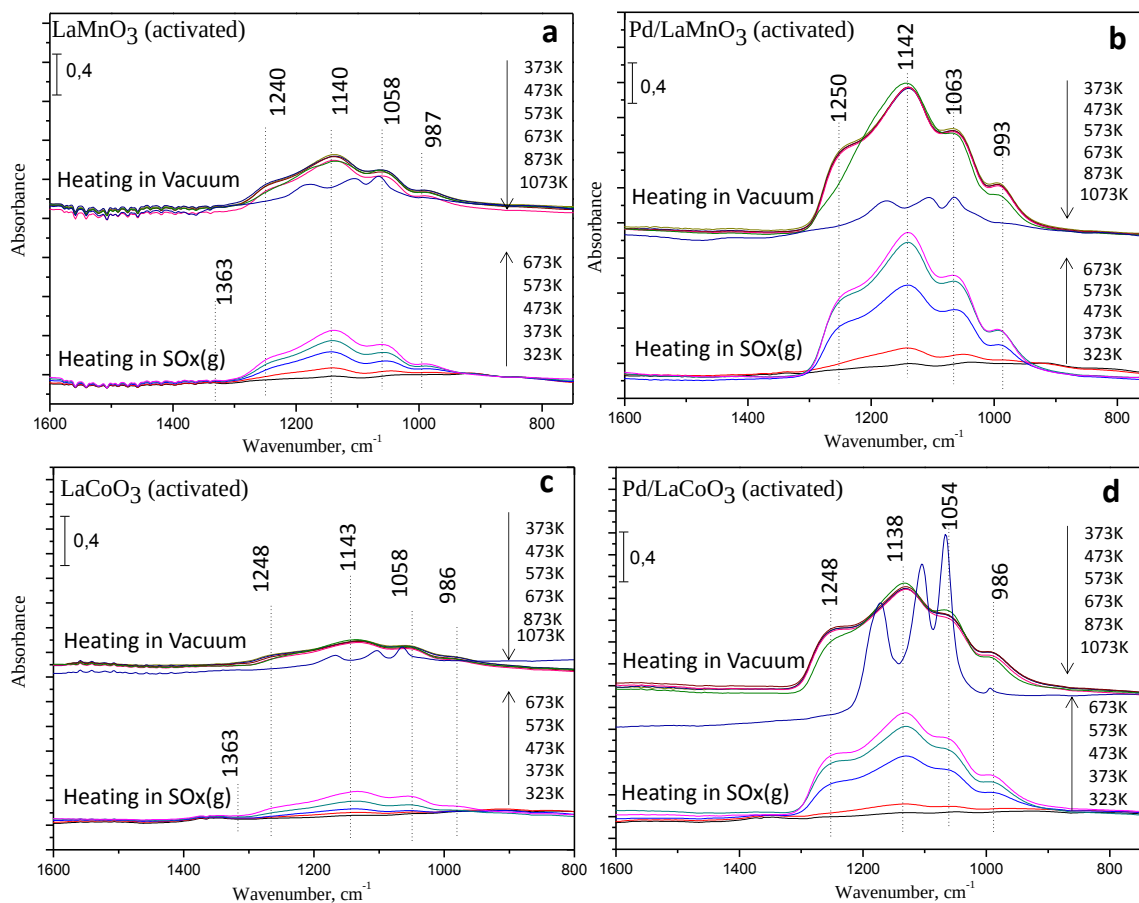


Figure 48. FTIR spectra related to SO_x uptake and release properties of a) LaMnO₃, b) Pd/LaMnO₃, c) LaCoO₃ and d) Pd/LaCoO₃.

4.3.3. SO_x Reduction with H₂ (g) on Perovskite surfaces.

Removal of SO_x species on S-poisoned perovskite materials via reduction with H₂ (g) was investigated by in-situ FTIR spectroscopy over LaMnO₃, Pd/LaMnO₃, LaCoO₃ and Pd/LaCoO₃ as seen in Figure 49. The bottom set of FTIR spectra presented in Figure 49 were recorded at 323 K after the samples were exposed to 2.0 Torr of SO₂+O₂ gas mixture (SO₂:O₂ = 1:10) at 323 K and 673 K. Then, gas mixture was evacuated from the reactor and 2.0 Torr H₂ (g) was introduced over the S-poisoned samples at 323 K. The upper set of FTIR spectra were collected at 323 K after sample was heated under hydrogen atmosphere at 673, 773 and 873 K for LaMnO₃, Pd/LaMnO₃ (Figure 49a and Figure 49b) and at 673, 773, 873 and 973 K for LaCoO₃ and Pd/LaCoO₃ (Figure 49c and Figure 49d). For LaMnO₃, adsorbed

SO_x shows strong resistance towards reduction with H₂ upon heating at 773 K and the type of sulfur species that adsorbed on the surface does not change as shown in the upper set of spectra in Figure 49a. Most of the adsorbed sulfur species are removed at 873 K. On the other hand, surface sulfate/sulfite species on Pd/LaMnO₃ are relatively unstable toward reduction in H₂ atmosphere even at 673 K (Figure 49b). Adsorbed SO_x on Pd/LaMnO₃ are partially removed at 773 K and complete removal of sulfur species occurs at 873 K after treatment with H₂ (g). These results show that the promotion of palladium enhances the reduction of surface sulfate/sulfite species in the presence of H₂ (g) which can be accomplished by the dissociative chemisorption of H₂ on Pd sites and subsequent reduction of SO_x species by the H-spill over [93]. H₂-desulfation of Co-based perovskites are shown in Figure 49c and Figure 49d. The reduction of adsorbed SO_x was not observed for LaCoO₃ during heating up to 773 K unlike Pd/LaCoO₃. Pd incorporation helps to reduce sulfur species even at 673 K. This result is similar with Mn-based perovskites (Figure 49a and Figure 49b). It is important to notice that the baseline of the spectra for LaCoO₃ that were obtained after annealing at 873 K and 973 K in H₂ atmosphere change significantly. This is due to the instability of Co-based perovskites. LaCoO₃ is quite unstable under H₂ atmosphere and the perovskite structure decomposes into Co⁰/CoO/La₂O₃ [11, 21-24]. The destruction of the perovskite structure and formation of different oxides results in the distortion of the baseline in the FTIR spectra. This baseline distortion is also observed for Pd/LaCoO₃ but it is not as significant as LaCoO₃ because Pd has a positive role on structural integrity so it preserves the perovskite structure from decomposing into different phases as described in section 4.2.1.4. Unlike the Mn-based perovskites where almost all SO_x species are removed at 873 K (Figure 49a and 49b), LaCoO₃ and Pd/LaCoO₃ show a poor SO_x reduction performance in H₂ (g) (Figure 49c and 49d). Even after reduction at 973 K, there exists SO_x species remaining on the Pd/LaCoO₃.

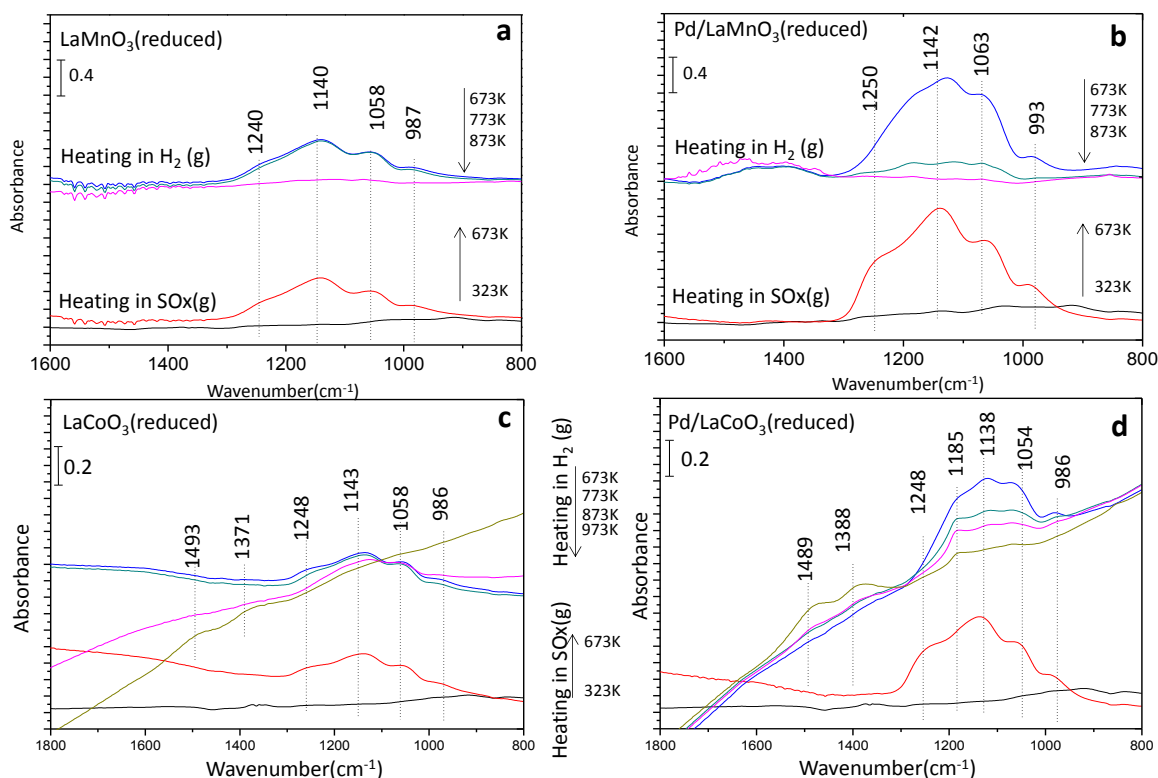


Figure 49. FTIR spectra related to the desulfation of a) LaMnO_3 , b) Pd/LaMnO_3 , c) LaCoO_3 and d) Pd/LaCoO_3 surfaces via $\text{H}_2(\text{g})$. Bottom set of spectra in each panel were acquired after SO_x exposure (2.0 Torr, $\text{SO}_2:\text{O}_2 = 1:10$) at 323 K, followed by annealing at 673 K in the SO_x gas mixture for 15 min. Upper set of spectra in each panel were acquired by heating at 673, 773 and 873 K under 2.0 Torr of $\text{H}_2(\text{g})$ for 15 min after SO_x gas mixture had been evacuated. All spectra were acquired at 323 K in vacuum.

4.3.4. Effect of S-poisoning on the NO_x Storage Capacity of Perovskites

The effect of Pd on sulfur uptake and release was discussed in the previous sections however, an important question that arises at this stage is that whether Pd sacrifices itself for additional sulfur uptake or whether sulfur is stored in a non-preferential manner on both Pd and perovskite sites. In order to find the presence of any preferential adsorption sites for sulfur, $\text{NO}_2(\text{g})$ was used as a probe molecule on poisoned material surfaces. Figure 50 shows the experimental results, in which the NO_x adsorption characteristics of fresh (Figure 50, black spectra) and S-poisoned (Figure 50, red spectra) LaMnO_3 (Figure 50a) and Pd/LaMnO_3 (Figure 50b) samples

were investigated in a comparative fashion under poisoning conditions (2.0 Torr $\text{SO}_2 + \text{O}_2$ gas mixture, $\text{SO}_2:\text{O}_2 = 1:10$ at 673 K, 30 min). The assignment of the nitrate/nitrite absorption on perovskites frequencies were mentioned in section 4.2.1.1 and Table 6. Figure 50 demonstrates that some surface NO_x species are changing after the poisoning of the LaMnO_3 and Pd/LaMnO_3 samples. Almost all of the NO_x species adsorbed on both fresh and poisoned LaMnO_3 surfaces are quite similar except the IR band at 1081 cm^{-1} (due to nitrite species on LaMnO_3 [17-20]) which is not present in the fresh sample (black spectrum in Figure 50a). For Pd/LaMnO_3 as seen in figure 46b, vibrational frequencies at 1322 cm^{-1} (due to nitrite species) and 1242 cm^{-1} (related to bidentate nitrates) diminishes whereas intensity of peak at 1280 cm^{-1} (related to monodentate nitrates) increases after poisoning the surface. This indicates that monodentate nitrate species are more favorable than bidentate ones on the poisoned surface due to the competition for adsorption sites between SO_x species and nitrates. Similar to the Pd-free counterpart, the IR peak at 1081 cm^{-1} due to nitrite species on LaMnO_3 also appears on the poisoned Pd/LaMnO_3 surface. Figure 50 clearly demonstrates that NO_x absorption intensities of fresh surfaces (black spectra) are higher than those of poisoned surfaces (red spectra). Suppression of the nitrate/nitrite intensities upon sulfur poisoning can be readily explained by the partial occupation of NO_x adsorption sites by thermodynamically more stable adsorbed sulfur oxide species [36]. As discussed in the previous sections, the NO_x storage capacity (NSC) of activated LaMnO_3 and Pd/LaMnO_3 are relatively similar to each other. This is also clearly visible when the black spectra in Figure 50a and 50b are compared. Figure 50a indicates that the IR bands associated with the NO_x species on the Pd-free LaMnO_3 sample have a characteristic attenuation upon S-poisoning. On the other hand, the Pd/LaMnO_3 sample (Figure 50b) reveals an even stronger attenuation than the LaMnO_3 sample. This observation strongly suggests that sulfur does not adsorb preferentially on the Pd sites where the perovskite and Pd sites are poisoned by S in a rather non-preferential manner.

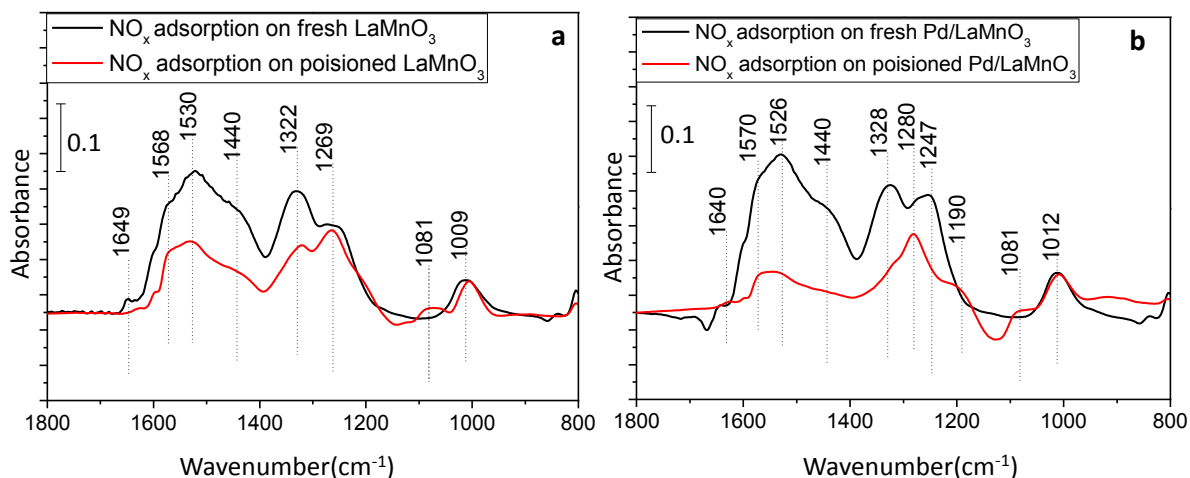


Figure 50. FTIR spectra acquired after NO₂ saturation (5.0 Torr NO₂(g), 323 K, 10 min) of fresh (black spectra) and S-poisoned surfaces (red spectra) via 2.0 Torr, 673K, SO₂:O₂ = 1:10. a) LaMnO₃ and b) Pd/LaMnO₃. All spectra were acquired at 323 K in vacuum.

An identical set of experiments was also performed for the Co-based materials (Figure 51). Nature of the adsorbed NO_x species do not change after LaCoO₃ is poisoned (Figure 51a). However, after sulfation of Pd/LaCoO₃, 1322 (due to nitrito species) and 1242 cm⁻¹ bands (related to bidentate nitrates) disappear with the formation of IR band located at 1293 cm⁻¹ (related to monodentate nitrates) (Figure 51b) because SO_x species block the active sites. Other results obtained from this set of experiments are rather identical to the findings obtained for Mn-based perovskites, suggesting the absence of a preferential sulfur adsorption site on the Pd/LaCoO₃ surface.

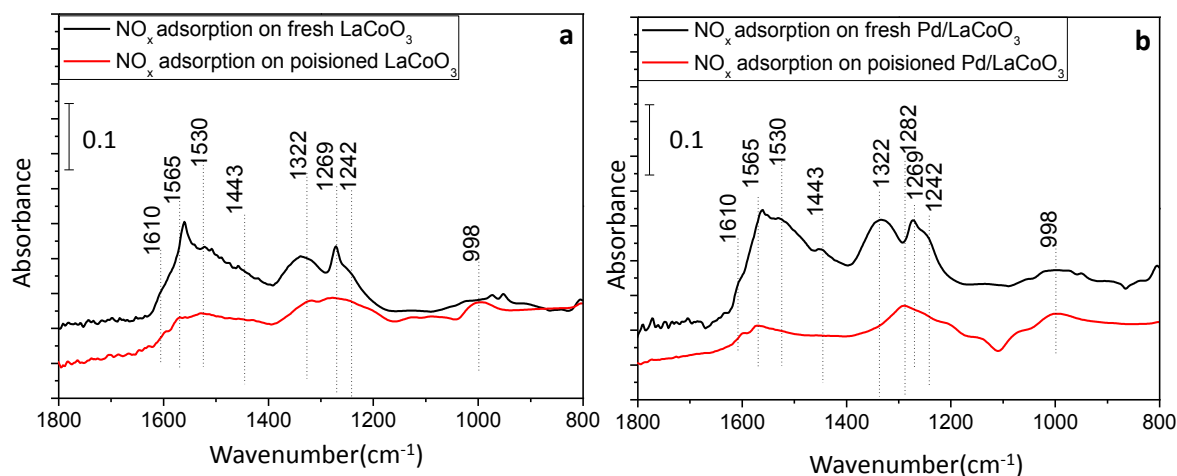


Figure 51. FTIR spectra acquired after NO_2 saturation (5.0 Torr $\text{NO}_2(\text{g})$, 323 K, 10 min) of fresh (black spectra) and S-poisoned surfaces (red spectra) via 2.0 Torr, 673K, $\text{SO}_2:\text{O}_2 = 1:10$. a) LaCoO_3 and b) Pd/LaCoO_3 . All spectra were acquired at 323K in vacuum.

4.4. Quantitative SO_x Uptake Determination via XPS

In order to provide a quantitative basis for the arguments discussed in relevance to the FTIR data given above, XPS measurements were performed on sulfated perovskite samples at 673 K and desulfated samples at 773 K via reduction with H_2 .

Figure 52 shows the relative surface atomic ratios of Mn/La and S/La that were investigated in the XPS analysis of the Mn-based samples. The FTIR spectra indicated in the Figure 52 are specific for XPS measurements. The surface S/La ratio slightly decreases after reduction of the sulfur species adsorbed on LaMnO_3 . However, it is clearly observed that the decrease in the amount of SO_x species after the reduction of perovskite with H_2 (g) is more pronounced for Pd/LaMnO_3 . The S/La ratio for sulfated Pd/LaMnO_3 is 0.80 whereas after reduction this ratio becomes 0.43. In other words, almost half of the surface sulfate/sulfites for Pd/LaMnO_3 are removed after reduction at 773 K in H_2 atmosphere. These results are in very good agreement with the corresponding FTIR data that shown in Figure 52.

The surface atomic ratios of Co/La and S/La for sulfated and reduced Co-based perovskites are shown in Figure 53. Similar to Figure 52, the FTIR spectra presented

in Figure 53 belong to samples that were used in the XPS measurements. Reduction of SO_x species adsorbed on LaCoO_3 does not change the amount of the stored SO_x species as seen in Figure 53. However, in the presence of Pd, reduction of SO_x with H_2 (g) causes a significant decrease in the surface sulfur. More than half of the surface SO_x species adsorbed on Pd/LaCoO_3 were removed in the presence of H_2 (g). Also it is worth mentioning that the changes of the Co/La ratio during reduction for LaCoO_3 and Pd/LaCoO_3 are completely different. This is due to the unstable lattice structure of Co-based perovskites as mentioned in section 4.2.1.1.

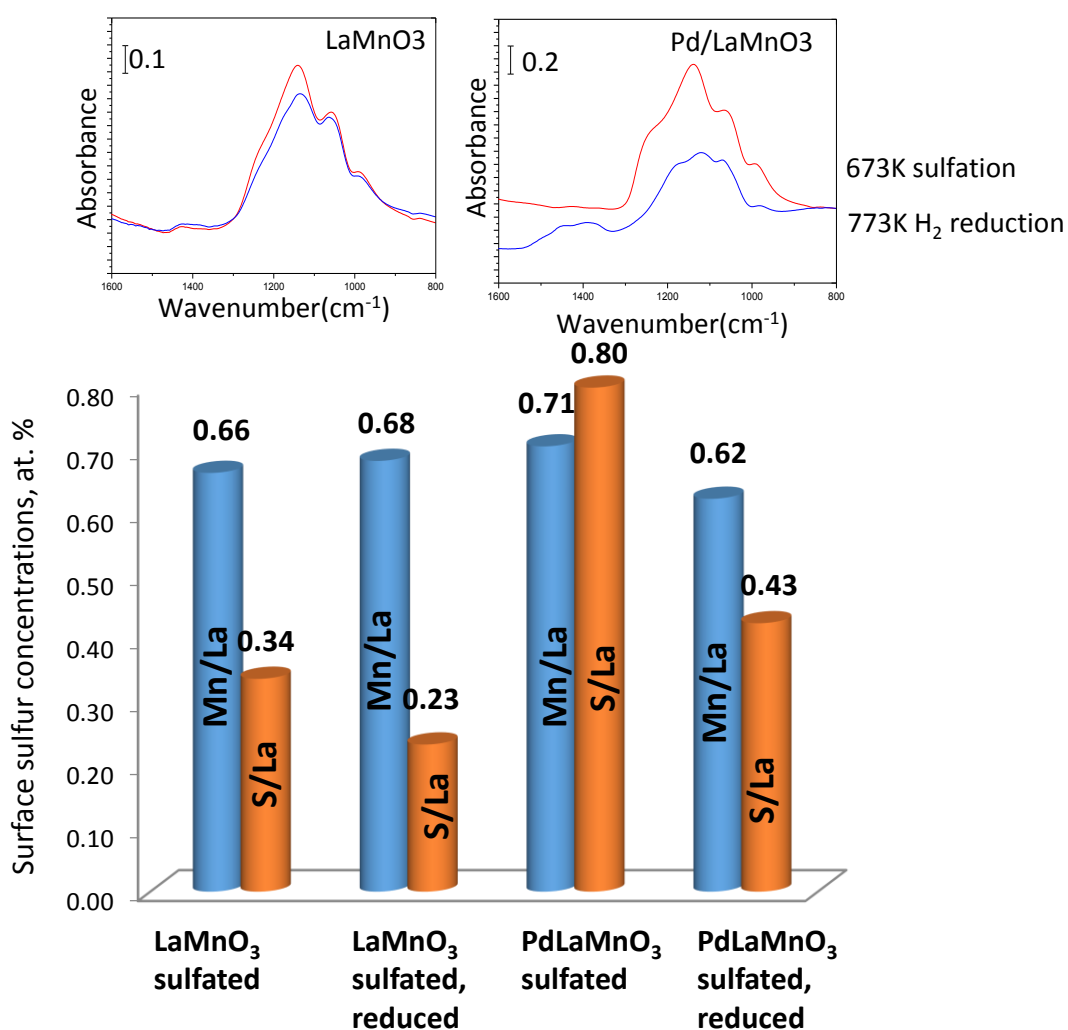


Figure 52. Surface atomic ratios for sulfated and sulfated+reduced LaMnO_3 and Pd/LaMnO_3 samples via XPS.

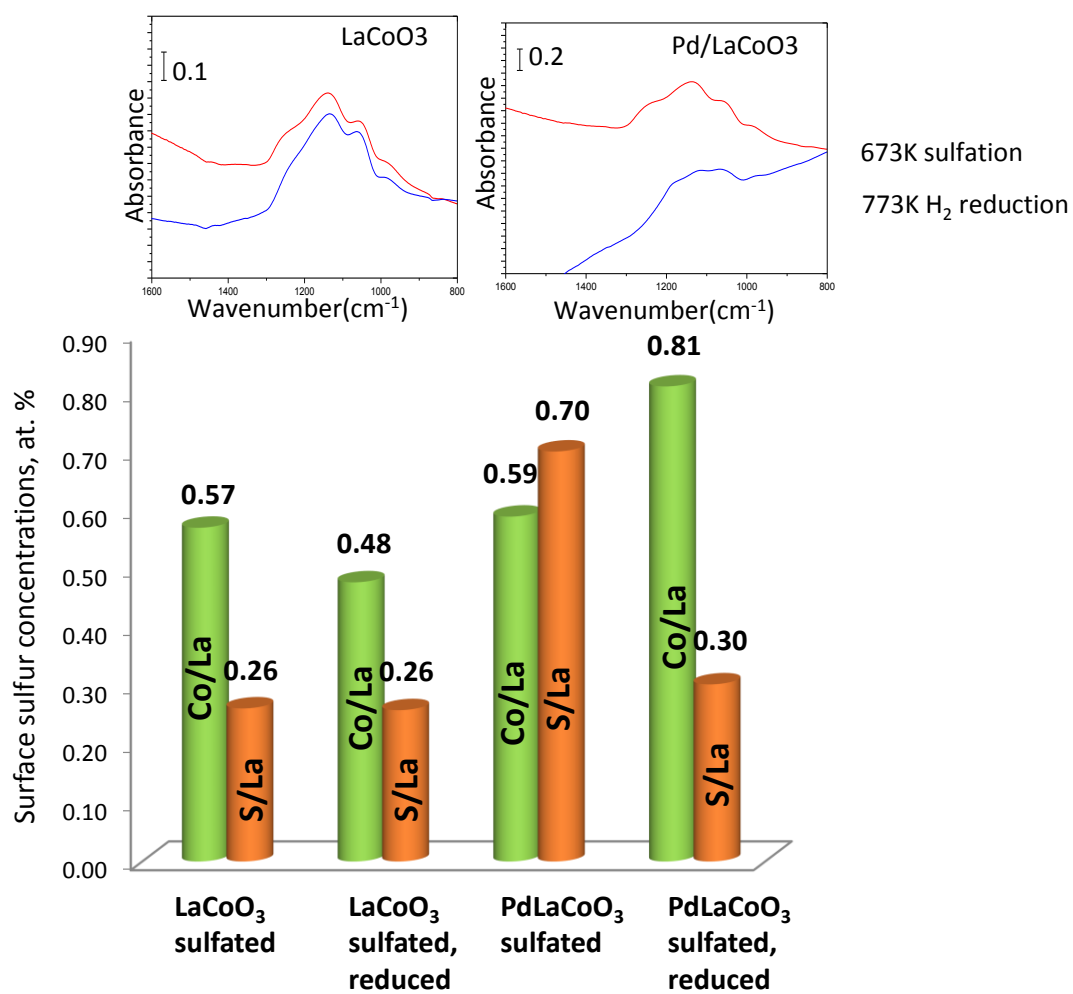


Figure 53. Surface atomic ratios for sulfated and sulfated+reduced LaCoO_3 and Pd/LaCoO_3 samples via XPS.

CHAPTER 5

5. Conclusions

In the current work, perovskite-based materials (LaMnO_3 , Pd/LaMnO_3 , LaCoO_3 and Pd/LaCoO_3) were synthesized, characterized and their NO_x uptake behavior was investigated as a function of the nature of the B-site cation (i.e. Mn vs Co), Pd incorporation and H_2 -pretreatment. Moreover, extent of sulfur poisoning of these materials was determined. Some of the major findings of the current study can be summarized as follows:

- LaMnO_3 and Pd/LaMnO_3 revealed a cubic perovskite crystal structure, whereas LaCoO_3 and Pd/LaCoO_3 exposed both cubic and rhombohedral phases after synthesis and calcination at 973 K.
- SSA values for LaMnO_3 and Pd/LaMnO_3 were significantly higher compared to that of LaCoO_3 and Pd/LaCoO_3 (20.6 and 21.9 m^2/g versus 7.1 and 8.9 m^2/g , respectively).
- Surfaces of all samples were found to be La-enriched either due to the presence of amorphous surface La_2O_3 domains or La-terminated ABO_3 structure.
- NSC of LaMnO_3 was found to be significantly higher than LaCoO_3 , in line with the higher SSA of LaMnO_3 .
- Incorporation of Pd nanoparticles with an average diameter of 4-5 nm did not have a significant effect on the NSC of fresh LaMnO_3 and LaCoO_3 .
- TPD experiments suggested that saturation of fresh LaMnO_3 , Pd/LaMnO_3 , LaCoO_3 and Pd/LaCoO_3 with NO_2 at 323 K resulted in the desorption of NO_2 , NO, N_2O and N_2 (without O_2) below 700 K, while above 700 K, NO_x desorption was predominantly in the form of $\text{NO}+\text{O}_2$.
- Perovskite materials were found to be capable of activating N-O linkages typically at c.a. 550 K (even in the absence of an external reducing agent such as H_2) forming N_2 and N_2O as direct NO_x reduction products.
- H_2 -pretreatment yielded a drastic boost in the NSC of all samples, particularly for the Co-based systems. Presence of Pd further boosted the NSC of the H_2 -pretreated samples.

- Increase in the NSC of H₂-pretreated LaCoO₃ and Pd/LaCoO₃ surfaces could be associated with the electronic changes (i.e. reduction of B-site cation), structural changes (surface reconstruction and SSA increase), reduction of the precious metal oxide (PdO) into metallic species (Pd) and the generation of oxygen defects on the perovskite. Mn-based systems were found to be more resilient towards B-site reduction.
- Pd-addition was found to suppress the B-site reduction and preserved the ABO₃ perovskite structure.
- H₂-induced increase in the NSC of the investigated perovskites render these materials as very promising systems to be used in NSR/LNT applications where the NSC can be periodically boosted on-board via periodical reducing (rich) cycles.
- Sulfur uptake capacity of LaMnO₃ is greater than that of LaCoO₃.
- SO_x uptake capacity significantly increases in the presence of Pd for both Mn- and Co-based perovskites.
- Although Pd/LaMnO₃ stores more SO_x, it releases sulfur species easily with thermal treatment. The release of SO_x species is reversible for Mn-based perovskites whereas it is irreversible for Co-based ones.
- Sulfur species adsorbed on LaMnO₃ and LaCoO₃ are quite stable during thermal treatment in H₂ atmosphere. On the other hand, thermal stabilities of SO_x species for Pd-containing perovskites are significantly lower so they can be easily regenerated in the presence of H₂(g).
- These results suggest that Pd-promoted Mn-based perovskite systems are promising oxidation catalysts revealing high NO_x oxidation capability, high NSC and enhanced sulfur tolerance.

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