

PREPARATION OF METAL/GRAPHENE COMPOSITES FOR AMMONIA
DECOMPOSITION REACTION



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Preparation of Metal/Graphene Composites for Ammonia Decomposition Reaction

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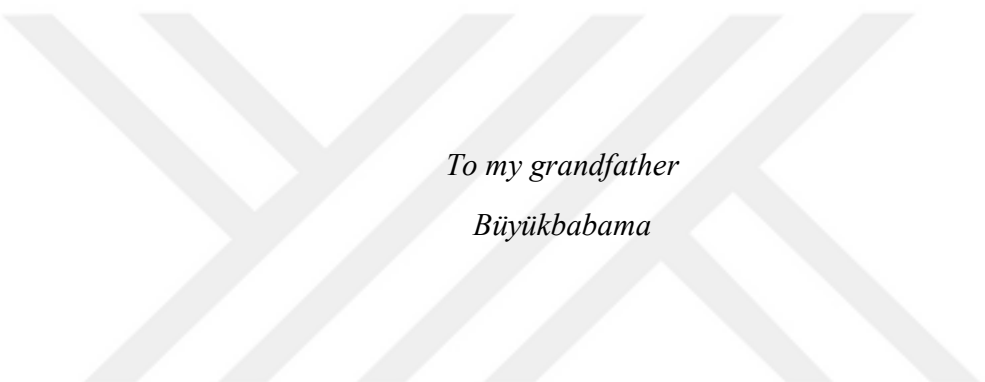
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To my grandfather
Büyükbabama

ABSTRACT

Currently, fossil fuels are the main source of energy, and it is known that these resources will not be available in the near future. Besides their limited nature, when they are burned, fossil fuels release gases harmful to the environment, and human health¹. This situation leads humanity to seek alternative, cleaner, and sustainable energy sources. At this point, hydrogen energy is a promising alternative due to its high energy release in a combustion reaction, and the reaction's clean nature². However, storage and transportation of hydrogen require high pressure or low temperatures. It is not safe and economically feasible. To overcome this issue, one of the solutions is to use hydrogen chemically stored in compounds for further decomposition. Ammonia is a promising hydrogen source because it contains 17.7% hydrogen by mass, is liquid at room temperature (8-10 bar), has well-known production procedures, easier access, and its health risks, and treatment are well known³.

The decomposition of ammonia requires catalyst surfaces, especially at low temperatures and pressures. Various metal catalysts have been extensively studied for catalytic ammonia decomposition. Ruthenium is known to be the most active catalyst for the reactions, but it is expensive and rare. As alternatives, nickel, iron, and cobalt are also known as active metals¹. In a catalytic reaction system, the dispersion of metal catalyst on a high surface area with appropriate electronic properties is necessary for efficient conversion. In the literature, various catalysts such as metal oxides or carbonaceous supports have been extensively studied. Graphene with excellent chemical and electrical properties is one of the promising supports for metals for ammonia decomposition reaction. Furthermore, graphene aerogel, a 3D structure with a very high surface area and conductive surface is an excellent candidate as support for metals in catalytic reactions.

In this thesis, metal loaded graphene aerogels are investigated for ammonia decomposition reaction. Graphene oxide precursor is synthesized via the modified Hummers' method. Graphene aerogels are prepared via three-step synthesis; hydrothermal treatment of graphene oxide solution, supercritical carbon dioxide drying, and thermal reduction. An additional impregnation step is used for metal loadings. The relationship between the concentration of impregnation solution and metal loadings on graphene aerogels are examined. Graphene aerogel loaded with 21.33% Iron catalysts achieved 100% ammonia conversion at 600 °C. The effect of alkali metals as a promoter in ammonia decomposition reaction has also been investigated. However, the addition of alkali metals to the iron/graphene aerogel system decreased the conversion. In addition, Iron/graphene aerogel system showed high stability, as long as 36 hours at 600 °C. Cobalt catalyst on graphene aerogel is also examined for ammonia conversion reaction. The cobalt/graphene aerogel system converted as high as 87.7% of ammonia at 600 °C. In contrast to the Iron catalyst, Cobalt catalysts had an unstable conversion that showed sharp decreases in conversion in few minutes. Lithium addition to cobalt catalyst significantly increased the conversion. However, alkali metal addition did not solve the instability.

ÖZETÇE

Günümüzde fosil yakıtlar ana enerji kaynağı olarak kullanılmakta, yakın gelecekte bu kaynaklara erişim olmayacaktır. Sınırlı olmasının dışında, yakıldığında, fosil yakıtlar çevre ve canlıların sağlığına zararlı gazların salınmasına neden olur¹. Bu durum insanlığı, temiz ve sürdürülebilir alternatif enerji kaynaklarının araştırmasına yönlendirmiştir. Bu noktada hidrojen enerjisi yakıldığında ortaya çıkan yüksek enerji ve temiz bir kaynak olması sebebiyle alternatifler arasında öne çıkmaktadır². Ancak, hidrojenin depolanma ve lojistiğinin sağlanması için çok düşük sıcaklıklar veya yüksek basınçlı sistemler gereklidir. Bu sistemler ekonomik açıdan uygulanabilir olmamasının dışında tehlikelidir. Bu sorunun üstesinden gelebilmek adına, önerilen çözümlerden biri hidrojenin daha sonra parçalanma reaksiyonları ile elde edilmesi üzere kimyasallar içinde depolanmasıdır. Amonyak hidrojen içeren kimyasallar arasında, ağırlığının %17,7'sinin hidrojen olması, oda sıcaklığında sıvı olması (8-10 barda), bilindik üretim sürecine sahip olması ve risklerinin iyi bilinmesi sebebiyle öne çıkmıştır³.

Özellikle düşük sıcaklık ve basınçta amonyak parçalama reaksiyonunun gerçekleşebilmesi için katalizör yüzeyine ihtiyaç duyulmaktadır. Çeşitli metallerin katalitik aktivitesi kapsamlı bir şekilde incelenmiştir. Bu reaksiyon için bilinen en aktif katalizör rutenyumdur, fakat rutenyum nadir ve pahalı bir metaldir. Alternatif olarak, nikel, demir ve kobalt metallerinin de katalitik aktivitesi olduğu bilinmektedir ¹. Bir katalitik reaksiyon sisteminde, metal katalizörün yüksek yüzey alanı üzerinde dağılımı ve uygun elektronik özelliklerin sağlanması dönüşümün gerçekleşmesi için gereklidir. Literatürde metal oksit veya karbon bazlı olmak üzere katalizör destek malzemeleri kapsamlı bir şekilde incelenmiştir. Grafen sıra dışı kimyasal ve elektriksel özellikleri sayesinde ümit vadeden katalizör destek malzemeleri

arasındadır. Ek olarak, yüksek yüzey alanına sahip ve elektrik iletkeni 3B bir yapı olan grafen aerogel katalitik reaksiyonlarda destek malzemesi olmak için mükemmel bir adaydır.

Bu çalışmada metal yüklü grafen aerojellerin amonyak parçalama reaksiyonundaki katalitik aktiviteleri incelenmiştir.

Grafen oksit öncül malzemesi modifiye Hummers' metodu ile sentezlenmiştir. Grafen aerojeller üç aşamalı bir sentez ile hazırlanmıştır; grafen oksitin hidrotermal reaksiyonu, süper kritik karbon dioksit ile kurutma ve termal indirgenme. Ek olarak metal yüklemeleri için daldırma yöntemi eklenmiştir. Daldırma çözeltilerinin derişimi ile metal yükleme oranlarının bağlantısı incelenmiştir. 600 °C sıcaklıkta %21.33 demir yüklü katalizör %100 amonyak çevirimine erişmiştir. Alkali metal katkısının katalitik aktiviteye etkisi de incelenmiş fakat, bu eklemenin katalitik aktivitede düşüşe sebep olduğu gözlemlenmiştir. Ayrıca, Demir/grafen aerogel sistemi yüksek stabilite göstermiş olup 600 °C sıcaklıkta 36 saat stabil kalmıştır. Grafen aerogel destekli kobalt katalizörün de amonyak parçalama reaksiyonundaki performansı ölçülmüştür. Kobalt/grafen aerogel sistemi ise 600 °C sıcaklıkta %87.7 amonyak dönüşümüne ulaşabilmiştir. Demir yüklü katalizörlerin aksine, kobalt katalizörlerde stabil olmayan dakikalar içerisinde keskin düşüşlerin olduğu bir dönüşüm izlenmiştir. Kobalt katalizörlerine lityum eklemesi amonyak dönüşümünde önemli bir artış göstermiş fakat stabilite sorununa çözüm olamamıştır.

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ABBREVIATIONS

AFM: Atomic Force Microscope

ATR-IR: Attenuated Total Reflectance – Infrared spectroscopy

BET: Brunauer – Emmett – Teller

FESEM: Field Emission Scanning Electron Microscope

GA: Graphene Aerogel

GC: Gas Chromatograph

GO: Graphene Oxide

MFC: Mass Flow Controller

SEM: Scanning Electron Microscope

TCD: Thermal Conductivity Detector

TGA: Thermogravimetric Analysis

XRD: X-ray Diffraction

XPS: X-ray Photoelectron Spectroscopy

Chapter 1: Introduction

1.1. Hydrogen Energy, Storage, and Economy

With the increase in population, demand for energy is increasing too. Today, the main energy sources are carbon based⁴. Carbon-based energy sources are limited in the earth, and when burned they emit CO, and CO₂ which are leading causes of air pollution, and global warming⁵. Because of this situation, seeking alternative, clean, and sustainable fuel is initiated. The idea of hydrogen as the fuel of the future is proposed. Hydrogen has the highest calorific value along with being the lightest element in nature⁴. This means high gravimetric energy density. Additionally, when burned, hydrogen does not generate CO or CO₂ like carbon-based fuels, only waste of hydrogen is water^{4,6}. When consumed, 1kg hydrogen can generate up to 120 MJ energy^{4,5}. This value is significantly higher than conventional carbon-based fuels such as natural gas (47 MJ), gasoline (43 MJ), and coal (23 MJ)⁴.

One of the reasons why hydrogen is not the main energy source today is its production is significantly more expensive than carbon-based fuels⁷. Another reason is the storage of hydrogen. Research on safe, and cost-efficient storage of hydrogen because of its high explosiveness is continuing. Hydrogen can be stored in gas, liquid, or solid media⁴. Storage in gaseous form requires extreme points of high pressure and low temperature^{4,8}. In the gas phase, its density of hydrogen is 0.089 kg/m³, which makes it prone to leakages⁴. Manufacture expenses of hydrogen proof vessels are very high, which is not feasible⁴. Storage of hydrogen in the liquid phase has its struggles. Maintaining liquid hydrogen in vessels require extremely low temperatures^{6,9}. This is highly inefficient; cooling the vessel consumes 30% of the energy of the stored hydrogen⁴. This damages the efficiency and potential of liquid hydrogen. Another proposition is the storage of hydrogen in the solid-

state. According to the claim, hydrogen-containing solids can be used as hydrogen storage materials. In the solid-state, volumetric, and gravimetric hydrogen content increases, when needed hydrogen can be extracted by certain methods. In the solid-state, hydrogen can be physisorbed or chemisorbed to the material^{4,10,11}. Heat treatment is needed to release physisorbed hydrogen from the material⁴. To increase the efficiency, high surface area materials need to be used such as metal-organic frameworks, covalent-organic frameworks, carbon nanotubes, and zeolites⁴. Hydrogen storage with chemisorbed hydrogen is made with complex hydrides or chemical hydrides such as NaAlH_4 ^{4,12}, and $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ ^{9,11}. Because of the irreversibility of hydrogenation, and reaction dynamics, it is unfeasible⁴. Metal hydrides are more feasible, because of the reversibility of hydrogenation, and operating temperatures close to room temperature. However, low hydrogen content and slow release of the hydrogen are metal hydrides' disadvantages. On the other hand, ammonia contains 17.7% hydrogen by mass, and become liquid in 8-10 bars at room temperature³. This makes ammonia a promising hydrogen source. Ammonia decomposition reaction converts ammonia to hydrogen, and nitrogen only. However, this reaction requires high temperatures, consequently an efficient catalyst. In Figure 1, a summary of hydrogen-containing materials in terms of gravimetric, and volumetric hydrogen density are given. Among the carbon-free hydrogen sources, liquid ammonia is one of the hydrogen dense materials.

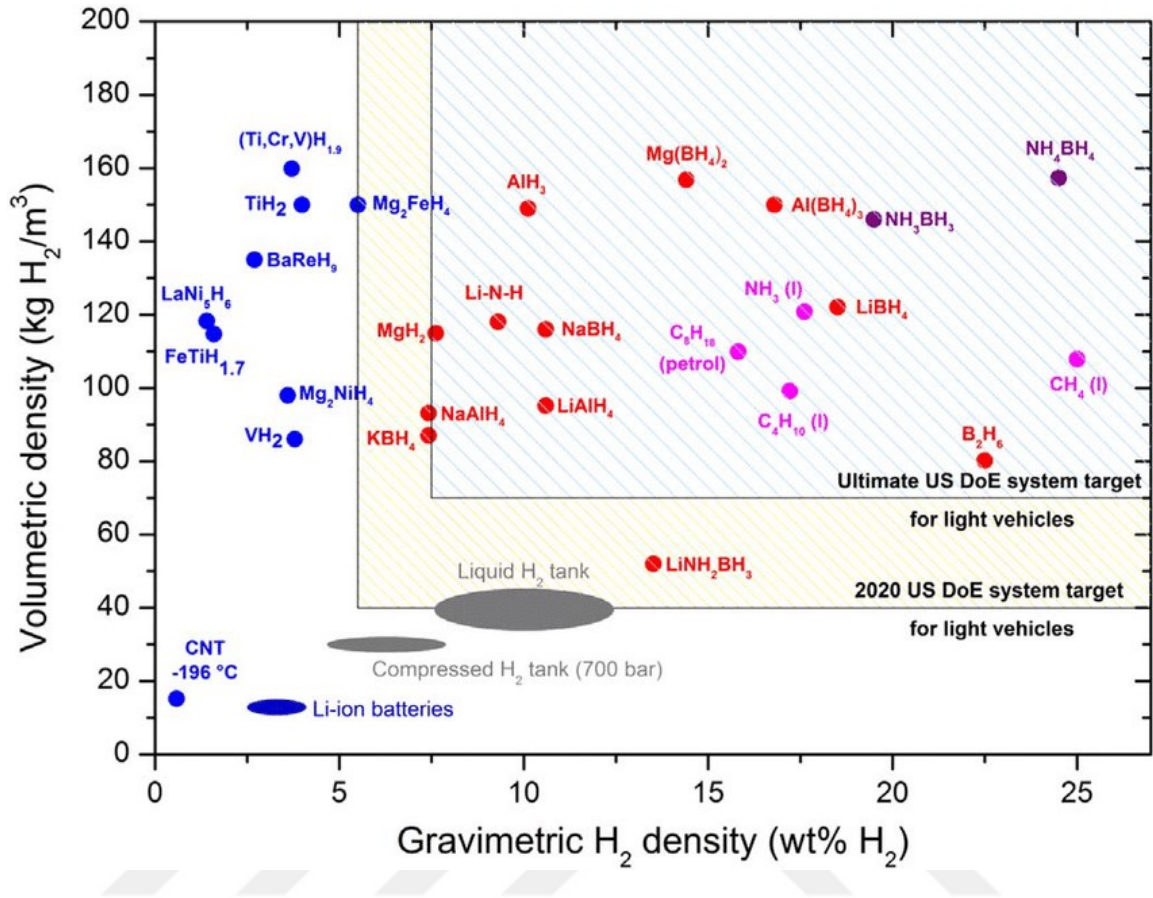


Figure 1: An overview of hydrogen sources in terms of gravimetric, and volumetric hydrogen density²

The hydrogen economy is the model that has hydrogen as the main energy source. To utilize this model, production of hydrogen needs to be produced efficiently, and at high volume⁴. Gaseous hydrogen has a low flash point, which makes logistics, and storage a struggle. Additionally, gaseous and liquid hydrogen storage are not financially reliable⁷. For improving the safety of storage, and logistics, hydrogen dense storage materials, and safer methods are proposed. Researches on solid-state, and ammonia-based hydrogen storage showed high amounts of hydrogen could be stored safely.

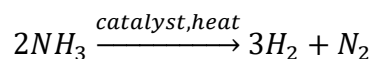
Although the hydrogen economy is based on environmental reasons, there are still obstacles present before it is implemented. The main barriers are storage, logistics, and lack of infrastructure.

1.2. Ammonia Decomposition

The pursuit of a clean, and efficient source of energy has resulted in the growth of attention for reliably produce, and store hydrogen². To achieve this goal, hydrogen production should also be clean for the environment. Popular production methods are steam methane reforming, coal gasification, electrolysis, thermochemical methods, and biomass gasification¹³. Several methods are suggested to improve conventional methods, that used electrical, photonic, thermal, and biochemical energy sources to convert water, fossil fuels, and biomass into hydrogen. Examples to these methods are thermolysis of water, plasma arc decomposition of fossil fuels, thermochemical biomass conversion, dark fermentation, biophotolysis etc¹⁴. Methods convert biomass, and fossil fuels to hydrogen also emit carbon dioxide, which contradicts the main focus of clean energy¹⁴. Processes that require water need improvement of efficiency, production rate, and separation methods¹⁴. Dark fermentation, biophotolysis, and photofermentation are also options for hydrogen production¹⁴. These methods have disadvantages, such as byproducts, large surface area requirements, and low production rates.

Storage is another challenge for the usage of hydrogen in daily life. Per gram, hydrogen has the best calorific value among the fuels¹⁵. However, the volumetric energy density of hydrogen is too low that storage needs to increase its density¹⁶. To store hydrogen as a fuel, compressed, cold compressed, and liquefied pure hydrogen gas are suggested¹⁷. Their volumetric energy densities are not enough to compete with conventional fuels either. Chemical storage of hydrogen is another option. Metal hydrides, complex hydrides, hydrogen adsorbed materials, and hydrogen in chemicals offer higher density hydrogen^{15,18}.

Ammonia is a strong candidate for hydrogen storage because of its 17.7% hydrogen content by mass. Hydrogen can be produced by ammonia decomposition reaction. The following reaction does not generate any CO_x².



Relative to hydrogen, ammonia is not flammable or explosive. It is toxic at 2500 ppm concentration but detectable at even lower concentrations as surveys show 9-45 ppm initially irritated humans¹⁸.

For the decomposition of ammonia, metals such as iron, nickel, platinum, ruthenium, rhodium, iridium, cobalt, palladium, chromium, and manganese are used as single or multiple metal catalysts¹⁹. Among other metals, these metals showed higher ammonia conversion rates. In Figure 2A the relation between energy requirement of the ammonia decomposition and the rate constant is given. Parallel to the graph, high conversions are achieved with ruthenium, iridium, platinum, and palladium catalyst¹⁹. However, these metals are rare, and expensive. Instead of using expensive metals, research on cheaper iron, and nickel catalysts are intensified. In the study of Choudhary et al., various metals are used as catalysts on silica support²⁰. At 650 °C, under 6000 mL NH₃ g_{cat}⁻¹ h⁻¹ flow, 10%Ni/SiO₂, and 10%Ru/SiO₂ achieved 70%, and 99% ammonia conversion²⁰. In the same study, 10%Ir/SiO₂ converted 98% of the ammonia in the same flow rate at 700 °C²⁰. Torrente-Murciano et al showed that 7% cobalt catalyst on Ax-21 carbon converted 70% of the ammonia at 500 °C under 5200 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity²¹. Li et al. converted ammonia via Fe/SiO₂, their catalyst converted 100% ammonia at 650 °C under 30000 mL NH₃ g_{cat}⁻¹h⁻¹ space velocity²². Effects of support material and promoters are investigated in the study of Yin et al.. It is concluded

that alkali, alkali earth or earth metal addition may prevent sintering of the active metal, which increase the catalytic activity²³.

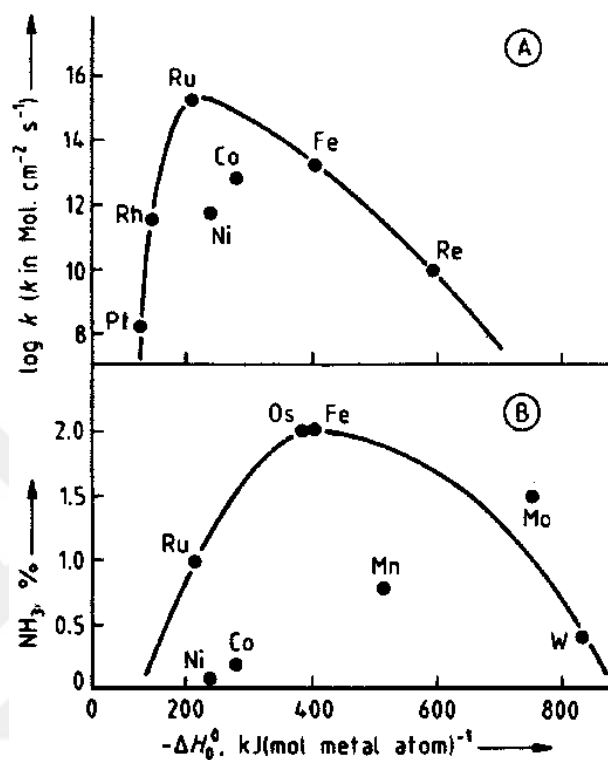


Figure 2: Logarithm of the rate constant of ammonia decomposition (A) and synthesis (B) reaction of metals as a function of $-\Delta H_f^\circ$ ⁰²⁴

Potassium addition dramatically increased the ruthenium catalyst's performance²⁵. Exposure of the active metals to reactants is a factor that directly affects the catalyst's performance. Good support material can help increase the exposure by high surface area¹⁹. Other essential properties of the support material are stability in reaction conditions, and electrical conductivity to ease the electron transfer during reaction¹⁹. Because of these reasons for the support materials for ammonia decomposition reaction such as carbon nanotubes are used. In this thesis, graphene aerogels with high surface area, and electrical conductivity are used to investigate the effect of these parameters on the catalyst's performance.

1.3.Graphene

Graphene is sp^2 hybridized mono layered carbon structure, which is the main building unit for carbon-based materials such as graphite. Due to extraordinary electrical, and mechanical properties of graphene, such as mechanical strength, flexibility, electrical conductivity, and high surface area, graphene and its derivatives are considered as a support material for different catalyst applications²⁶. There are two general methods to obtain graphene: bottom-up, and top-down. Bottom-up methods generate graphene by growing the crystal on a seed whereas, in the top-down method, layered carbon sources such as graphite chemically separated to its layers²⁶. In bottom-up methods, graphene layers are synthesized via adsorption of a precursor with desired functional groups on to a surface. Adsorption is followed by activation, polymerization, and cyclodehydrogenation in order to obtain graphene sheets²⁶. In the top-down method different strategy is employed to obtain graphene. Precursors which contain graphene as a building block are separated into graphene sheets in top-down methods via chemical or mechanical separation of the layers²⁶. During chemical separation of the layers desired properties, because of the chemical alteration of the surface loss of the desired properties of graphene is possible. In these cases, another step such as reduction is added to the method to remove the effects. For the top-down synthesis' final product, exfoliation methods are important. Parameters such as temperature, exfoliation method, and conditions, the synthesis method changes the product²⁶. By changing the parameters final product may be adjusted according to the need of the study. For exfoliation of graphene sheets, several methods are developed such as sonication, shear exfoliation, and microfluidization²⁶. Exfoliation with sonication separates the layers via intercalation of the solvent graphene layers²⁶. Shear exfoliation uses the same principle with sonication, however, in this method, rotating blades are used instead of ultrasound²⁶. Microfluidization

method separates layers via high pressured narrow chambers²⁶. In this thesis, graphene is synthesized from graphite via modified Hummers' method combined with exfoliation via sonication. Top-down methods may be used for forming 3D graphene structures because of the advantage of dissolved layers of graphene. As mentioned before, graphene and its derivatives are promising catalyst support materials because of the electrical and mechanical properties. Graphene aerogels are 3D structured graphene with low density and porous structure, which provides high accessible surface area. For ammonia decomposition reaction metal catalysts can be supported on graphene aerogels because of these electrical and mechanical properties. There is a number of metal loading techniques on graphene structures such as gas phase or chemical deposition^{23,26}. In this thesis, chemical loading of metals on graphene aerogel is used.

1.4. Graphene Oxide

In top-down methods, graphene oxide is synthesized first to obtain graphene. Unlike graphene, graphene oxide's structure is not planar. Because of the oxygen-containing groups on the surface, exfoliation in water is more feasible²⁶. This advantage in exfoliation is used to obtain graphene in the form of reduced graphene oxide. To synthesize graphene oxide, its precursor graphite needs to be oxidized. In the literature, different methods are suggested with strong oxidizing agents and their combinations²⁷. The first method introduced to synthesize graphite oxide was Brodie's method in 1860²⁸. In this method fuming nitric acid, and potassium chlorate are used. Because of the long reaction time, and emission of large amounts of toxic gases, improvement of the synthesis was necessary²⁹. In 1898 Staudenmaier developed a new method with the addition of concentrated sulfuric acid to Brodie method²⁹. Due to the slight change in the procedure, Staudenmaier's method was still toxic, and time-

consuming. In 1937 Hofmann used concentrated nitric acid instead of fuming nitric acid³⁰. Until Hummers, and Offerman introduced their relatively less time consuming, and safer method, Brodie's, Staudenmaier's, and Hofmann's methods were used²⁷. In Hummers' method, instead of nitric acid, and potassium chlorate, sodium nitrate, and potassium permanganate are used to oxidize graphite³¹. This method eliminated the chlorine-containing gas emission of the synthesis³¹. Manganese dioxide and permanganate ions produced during the synthesis can be eliminated via hydrogen peroxide addition, and washings³¹. Over time, Hummers' method was modified, and improved²⁷. In the version of Marcano et al., they used a mixture of sulfuric acid, and phosphoric acid to oxidize graphite³². This method yielded significantly less product compared to previous methods, but no nitrous gas emitted in the process³². Modified Hummers' method in Saraç Öztuna et al.'s article, is used in this study³³. In this variation, graphite is oxidized with concentrated sulfuric acid, sodium nitrate, and potassium permanganate. Hydrogen peroxide is used to remove excess permanganate ions, and manganese oxide remaining in the solution. To further removal of impurities, washings are made with hydrochloric acid, and water after every washing, solutions are centrifugated. Lastly, centrifugates are collected and dispersed in water. Graphene oxide is obtained via exfoliation of the dispersion, which contains graphite oxide in this stage.

There are two exfoliation methods for this synthesis; sonication, and electrochemical exfoliation. Sonication assisted chemical, and electrochemical exfoliation methods have differences in disruptiveness, and efficiency²⁶. Graphite, in dipolar aprotic organic solvents or water, can be exfoliated into graphene with low efficiency²⁶. In the case of graphite oxide, oxygen-containing groups shown in Figure 3 such as hydroxyl, epoxy, and carbonyl on the layers increases the hydrophilicity, and increase the chance of water intercalation between

layers with the assist of ultrasound³⁴. This intercalation results in better exfoliation efficiency, and dispersion stability.³⁴ Electrochemical exfoliation is made via applying a certain electrical potential to create intercalated graphite compounds³⁵. These compounds need thermal or electrical treatment to remove intercalated solvent molecules³⁵. In this study, sonication is used for exfoliation for synthesizing graphene oxide.

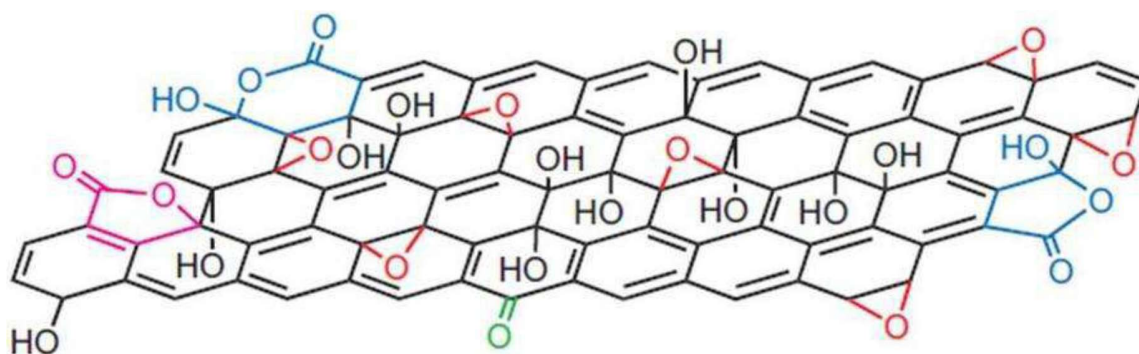


Figure 3: Structure of graphene oxide³⁶

1.5.Reduced Graphene Oxide

To convert exfoliated layers of graphene oxide to graphene a reduction is necessary for regaining properties of graphene lost after oxidation²⁶. There are ways to reduce graphene oxide such as chemical or thermal reduction²⁶. The chemical reduction can be conducted via reducing agents such as hydrazine³⁷, and sodium borohydride^{26,36}, organic acids such as L-ascorbic acid³⁸, alcohols such as methanol, and ethanol³⁹, metals such as zinc³⁸, sugars such as glucose, and fructose³⁸, and microbes such as E-coli, and yeast³⁸. Chemical methods are not ideal due to the possibility of leaving residue or dopants from reducing agents, especially metals while observing other metals' catalytic activities on reduced graphene oxide support^{37,38,40}. Some chemical methods may include toxic chemicals such as hydrazine.³⁸ Thermal reduction requires a reducing atmosphere and high temperatures. Besides, deoxygenating the carbon support, it helps to reduce the loaded metals to metallic state⁴¹.

The mechanism of thermal reduction is multistep and complex^{36,42}. Intercalated water present on graphene oxide because of the exfoliation and oxygen-containing groups on graphene oxide is removed in the reaction^{36,42}.

1.6. Graphene Aerogel

Graphene aerogel is a highly porous material consists of randomly stacked graphene sheets.²⁶ Its porous structure provides enough surface area to use it as a support material for catalytic reactions. To synthesize graphene aerogels, graphene oxide solution, which has a concentration of 3.0 g/L, undergoes a one-step hydrothermal reaction at 180 °C for 3 hours⁴¹. The result of this reaction is called a hydrogel. The hydrogel is stable in water, and its pores are filled with water. In this stage, a drying procedure would cause the collapse of the pores due to capillary pressure⁴³. To prevent the collapse of hydrogels', solvent was exchanged with ethanol due to its solubility in supercritical CO₂⁴⁴. Hydrogels are called alcogels after solvent exchange. In this thesis, graphene aerogels are loaded with iron, and cobalt via the impregnation method. To load the metals onto the support material, alcogels dipped into iron, and cobalt precursor solutions. Precursor solutions are Fe(NO₃)₃·9H₂O in ethanol, and Co(NO₃)₂·6H₂O in ethanol. In order to control the metal loading ratio, a gradient of precursor solution concentrations used. After this impregnation samples are dried with supercritical CO₂ drier at 50 °C, under 120 bar pressure for 2 hours. Thermal reduction applied to the samples in order to remove oxygen and reduce the loaded nanoparticles.

Thermogravimetric analysis is conducted under air. According to the remaining powder's XRD pattern, only natural metal oxides (Fe₂O₃, Co₃O₄) remained in the sample holder. The back-calculation is made to find the actual metal loading percentage. XRD of thermally reduced samples shows that iron and cobalt are present in their metallic form.



Chapter 2: Synthesis and Characterization of Graphene Aerogel

2.1. Introduction

Aerogels are a highly porous solid network of particles filled with air⁴⁵. Because of the porous structure, the surface area of the aerogels is high⁴⁶. For the production of aerogels, a 3D network of the solid needs to be constructed in a liquid medium, the liquid portion of the mixture then removed to obtain aerogels⁴⁶. Graphene aerogels are the aerogels constructed with randomly stacked graphene sheets. There are several different approaches for the 3D structure formation and drying of graphene aerogels. Graphene aerogels can be formed via hydrothermal reduction, metal-induced reduction, chemical reduction self-assembly, and ice-templating^{26,47}. The main reaction mechanism in all methods is the random stacking of partially or fully reduced graphene oxide⁴⁷. In this thesis, hydrothermal reduction method is used. Hydrothermal construction of graphene aerogel provides cross-linker and chemical-free catalyst support^{47,48}. After the construction of the 3D network, it is necessary to maintain the porosity during the removal of the solvent (drying). The drying method may affect the surface area via capillary forces during the extraction of the solvent which causes the collapse of the pores⁴⁹. Because of these capillary forces, conventional drying of the aerogels is not an option. There are two ways to dry the aerogels without collapsing the pores; freeze-drying, and supercritical CO₂ drying. Freeze drying procedure consists of two steps, freezing the liquid trapped in the solid network and with the help of vacuum, sublimating the frozen solvent. During the freeze-drying expansion or contraction of solvent's freezing, damages the pores of the aerogel⁵⁰. The damage causes an undesired decrease in the surface area. Instead, the usage of supercritical CO₂ drying does not generate any tension between pores, and solvent⁵¹. This technique requires a supercritical fluid which would act as a solvent for

the liquid. Organic solvents such as ethanol and acetone dissolve in supercritical CO₂⁴⁹. At 31.1 °C and 73.8 bar CO₂'s phase changes to a supercritical fluid. Because of the accessibility of these values, drying in CO₂ is plausible⁴⁹. However, the solvent between the pores of the 3D structure must be soluble in supercritical CO₂. Otherwise, the change of the liquid is necessary. This exchange of solvent can be carried out via storing the hydrogels (aerogels with water inside the pores) in the desired solvent such as ethanol or acetone for at least 36 hours. During the supercritical CO₂ drying, solvent between the pores applies no disturbance to the pores, maintaining the surface area of the 3D network. In this study, the 3D structure is constructed via hydrothermal reduction and supercritical CO₂ drying is utilized. Even if freeze-drying is easier and cost-efficient, because of the importance of the surface area, in this study drying with supercritical CO₂ is used. Furthermore, in the literature, surface area of freeze-dried graphene aerogels are significantly lower than supercritical CO₂ dried aerogels as expected^{51–53}.

Properties such as electrical conductivity, thermal, and electrical stability make carbon support materials attractive for catalyst applications^{2,54}. Aside from these properties carbon materials have distinct features such as easier metal reduction on the support, versatile physical shape (flakes, powders, granules, etc.), low production cost compared to silica or alumina, and high stability in high or low pH⁵⁵. Carbon supports are widely used and researched in the area of catalysis, due to the given properties. However, graphene stands out with its exceptional electrical, mechanical, and thermal properties among carbon-based supports. Because of the porous structure along with graphene's properties, graphene aerogels are also considered for these applications. When considered as a catalyst support graphene aerogels provide accessible surface for active sites of the catalyst. The increased

amount of accessible surface of support material results in better dispersion of the active material consecutively increased exposure of the reactants with the catalyst^{2,19}. On the other hand, catalysts can be used without support. However, the performances are not comparable with supported catalysts^{2,19,56}. The use of the support material helps to increase the surface area along with electrical conductivity provided by the support material, which ultimately increases the active sites exposed to reactants and electron transfer during the reaction⁵⁶.

The focus of this thesis is to determine the catalytic performance of graphene aerogel supported catalysts for ammonia decomposition reaction. The aforementioned properties of graphene and graphene aerogels are expected to show high performance when compared with similar active materials on different support materials. Ammonia decomposition reaction mechanism requires initial adsorption of N, followed by an N-H bond cleavage². During the adsorbed period active site of the catalyst is occupied, and cannot be in a reaction with another molecule². N-H bond cleavages form H₂ desorption of adsorbed N via the formation of N₂ releases the active site². This reaction requires high temperatures². Thus, a catalyst for the reaction should have high thermal stability. Graphene aerogels showed thermal stability after hydrothermal treatment or annealing⁴⁴. Carbon support materials such as carbon nanotubes, graphite or activated carbon are overshadowed by graphene's theoretical specific surface area of 2630 m² g⁻¹, and thermal conductivity of 5000 W m⁻¹ K⁻¹ ^{57,58}. Carbon nanotubes activated carbon, graphite, and fullerenes have a theoretical specific surface area of 1315, 1200, 10, 5 m² g⁻¹, and thermal conductivity of 3000, 0.5, 3000, 0.4 W m⁻¹ K⁻¹ respectively^{58,59}.

Carbon-based or oxide support materials are used as catalysts for the ammonia decomposition reaction. Li et al. showed the effect of surface area with Fe nanoparticles in

silica core-shells. Samples with higher surface area worked better as a catalyst in terms of ammonia conversion in the same conditions²². Podila et al. used MgO-La₂O₃ support material with cobalt loading, the surface area of the support materials are ranging from 33 to 86 m² g⁻¹⁶⁰. In different works, metal loaded support materials silica-alumina zeolites⁶¹, Ax-21 carbon²¹, titanate⁶², reduced graphene oxide⁶³ are used. The surface area of the catalysts remains under 350 m² g⁻¹ except for Ax-21 carbon.

In this chapter, graphene oxide is synthesized via modified Hummers' method. Graphene aerogels are constructed via hydrothermal reaction of the graphene oxide solution. Supercritical drying and thermal reduction of aerogels are conducted. Properties of the graphene aerogels investigated via structural characterization in order to understand its advantages as catalyst support.

2.2. Materials, and Procedure

2.2.1. Materials, and Equipment

99.9995% graphite produced by Alfa Aesar is used as a precursor. For the oxidation of graphite, NaNO₃ from Alfa Aesar, KMnO₄, and H₂O₂ (30%) from Merck Millipore, HCl, and H₂SO₄ (95-97%) from Sigma Aldrich are obtained. For solvent exchange 99% ethanol from Isolab. In all the procedures, distilled water with 18.2 MΩ resistance is used.

Bruker D8 X-ray Diffraction (XRD) equipped with Cu Kα X-ray source, Nicolet Attenuated Total Reflection-Infrared Spectrometer (ATR-IR), Micromeritics Brunauer – Emmett – Teller (BET), Bruker Atomic Force Microscope (AFM), Thermo Scientific X-Ray Photoelectron Spectrometer (XPS) equipped with Al Kα X-ray source, Reinshaw Raman equipped with 532 nm, 0.6 W laser, and Zeiss Scanning Electron Microscope (SEM) are used for characterizations.

2.2.2. Graphene Oxide Synthesis

In an ice bath, 3g graphite is added in the 138 of ml concentrated H_2SO_4 mixture having 3g NaNO_3 . 30 minutes after addition, 18g KMnO_4 is slowly added into the mixture with constant stirring. The ice bath is removed, the temperature of the reaction mixture is rose to 35°C by itself, and the reaction took place for 1 hour. The mixture was put into the ice bath again, and with 138 ml cold water, the reaction mixture is slowly diluted. Subsequently, the reaction mixture is removed from the ice bath. Temperature rose to 75°C and the reaction mixture was kept at this temperature for 30 minutes. After 30 minutes, reaction mixture air-cooled to room temperature, the addition of H_2O_2 is made until color changes to orange. Before exfoliation, the reaction mixture is centrifuged, washed 3 times with 5% HCl , and 3 times with distilled water. Centrifugates were collected in a total of 600 ml water. Collected mixture sonicated for 4 hours to assist exfoliation. The exfoliation mixture is centrifuged, and the resulting solution is called graphene oxide solution. To determine the concentration of the resulting mixture, 5 ml samples filtered through $0.45\ \mu\text{m}$ cellulose nitrate filter. Filtered substances are air dried at room. Dried graphene oxide is weighed to calculate concentration.

2.2.3. Graphene Aerogel Synthesis

Graphene aerogel is synthesized by the hydrothermal reaction of the graphene oxide solution as shown in Figure 4. Graphene oxide solution is diluted to 3 g/L. In a PTFE reactor, diluted graphene oxide solution is heated to 180°C for 3 hours. Layers of graphene oxide randomly bind with other layers of graphene oxide in this reaction, and this results in a porous 3D structure of graphene oxide. The reaction yields a structure that has pores filled with water and is stable in water called hydrogel. If hydrogels dried directly, water in the pores create a capillary effect and may break the layers, which cause shrinking, and loss of surface area⁴³.

In order to dry the hydrogels, their solvent is changed to a solvent that is soluble in supercritical CO₂ then that solvent is removed via supercritical CO₂ flow. Solvent exchange is made via placing the hydrogel into absolute ethanol for 36 hours, ethanol is replaced with fresh ethanol in every 12 hours. Dried products are called aerogels.

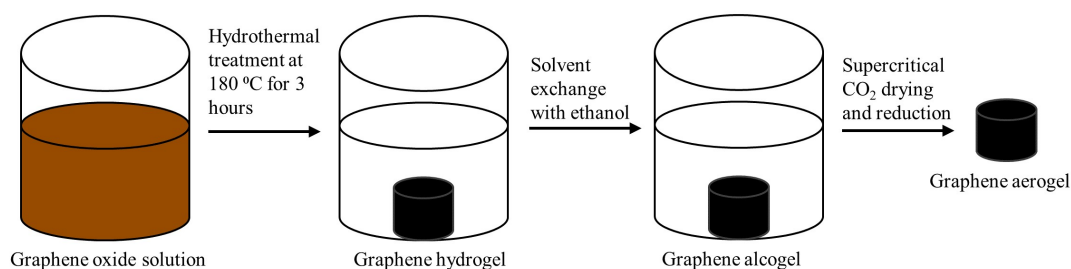


Figure 4: Graphene aerogel formation from graphene oxide solution

2.2.4. Thermal Reduction of Graphene Aerogels

To convert partially reduced aerogels to graphene aerogels, a further reduction is necessary. The thermal reduction is used in this thesis. Degasification is conducted at 110°C for 30 minutes under Ar flow. Reductions are taken place for 2 hours under 90%Ar, 10% H₂ flow at 600°C, and 700°C according to the sample.

2.2.5. Characterization of Graphene Oxide

The concentration of graphene oxide solution is determined via preparing graphene oxide films. Films are produced via vacuum filtration of 5 ml sample on 0.45 µm cellulose nitrate filter. Formed paper air dried, weighed to determine the concentration. The procedure repeated three times to increase accuracy. These films are also used for other characterization methods. XRD used for analyzing crystalline structure, and interlayer distance. XPS is used for analyzing surface chemistry. Raman is used for analyzing the defect ratio of the structure.

ATR-IR is used for the analysis of the functional groups on the papers. FESEM is used for the investigation of the morphology. AFM is used to analyze the sizes of the graphene sheets.

2.2.6. Characterization of Graphene Aerogels

XRD patterns are investigated to determine the crystal structure and interlayer distance. XPS is used to investigate surface chemistry. Raman is used for the investigation of defects. BET analysis is made to determine the surface area, and pore sizes of the aerogels. TGA is conducted with air to determine that in high temperatures plain aerogels do not leave any residue. TGA is also conducted under nitrogen to determine the weight loss caused by the reduction.

2.3. Results, and Discussion

2.3.1. Properties of Graphene Oxide Solution

For a deeper understanding of the graphene oxide, characterization methods are applied to graphene oxide or graphene oxide films. In this section, characterization results of graphene oxide presented and the changes between graphene oxide and graphite are discussed in terms of the success of graphite's oxidation. FESEM image of the graphene oxide film used in characterizations is given in Figure 5. The thickness of the film is 1.5 μm according to the SEM images.

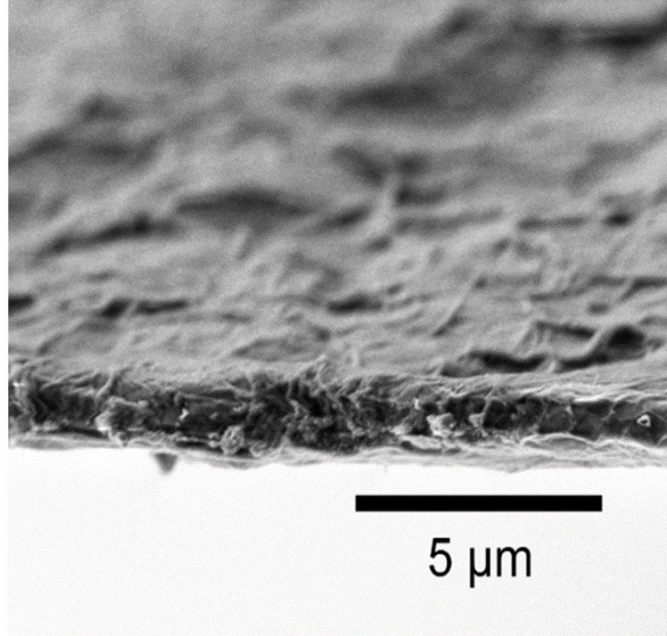


Figure 5: FESEM image of graphene oxide film

The interlayer distance of graphene oxide should be higher than graphite because of the oxygenated surface²⁶. To investigate this relation, XRD patterns are compared. Graphite's (200) peak on 26° in the XRD pattern yields a 0.337 nm interlayer distance. Interlayer distances can be calculated via Bragg's law, given below⁶⁴.

$$n\lambda = 2d\sin\theta$$

In the equation, n is the order of the diffraction, λ is the wavelength of the X-ray, d is the interlayer distance, and θ is the angle of the X-ray beam. In Figure 6, the XRD pattern of graphene oxide film synthesized via modified Hummers' method is given. By the sharp peak at 10.95° , interlayer distance is calculated as 0.81 nm. This increase confirms the oxygenated surface³³ and intercalated water between the graphene sheets⁶⁵.

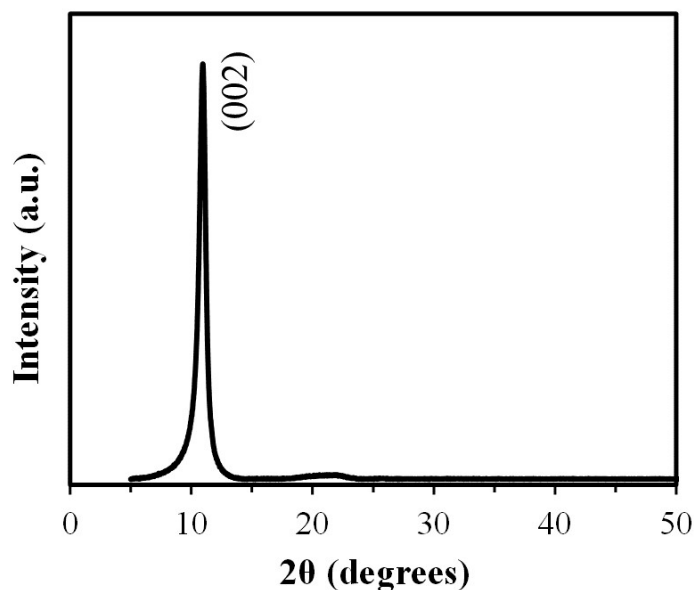


Figure 6: XRD pattern of graphene oxide film³³

The surface chemistry of the graphene oxide films is investigated via XPS. C1s and O1s XPS spectra are given in Figure 7 (a), and (b). In Figure 7 (a), the C1s spectrum is deconvoluted to three peaks at 284.5, 286.5, and 288.0 eV regarding carbon-carbon double, and single bonds, carbon-oxygen single bonds, and carbon-oxygen double bonds, respectively⁶⁶. The carbon-oxygen ratio on the sample is directly proportional to the signal intensity ratios of carbon-carbon bonds to carbon-oxygen bonds in the XPS C1s spectrum. These ratios also indicate the amount of oxidation or reduction. To understand the success of the oxidation of graphite, this connection can be used. Carbon-oxygen single bonds and carbon-oxygen double bonds signals' ratio to carbon-carbon bonds are 1.25, and 0.15 respectively⁶⁷. These ratios reveal that there is more carbon-oxygen bond than carbon-carbon bond. This means, oxidation of the graphite is successful. O1s spectrum of the sample is also investigated to confirm the successful oxidation and double and single bond ratio of carbon-oxygen bonds. O1s spectrum given in Figure 7 (b) deconvoluted to 3 peaks positioned at 531.0, 532.1, and

532.8 eV regarding oxygen double bound to aromatic carbon, oxygen single bound to aliphatic carbon, and phenolic oxygen⁶⁵. The peak intensities of the O1s spectrum also supports that carbon-oxygen double bonds are the less common species. Survey spectra of the synthesized graphene oxide is also given in the Figure 7. This spectra reveals that there are no impurities which may alter the course of procedures.

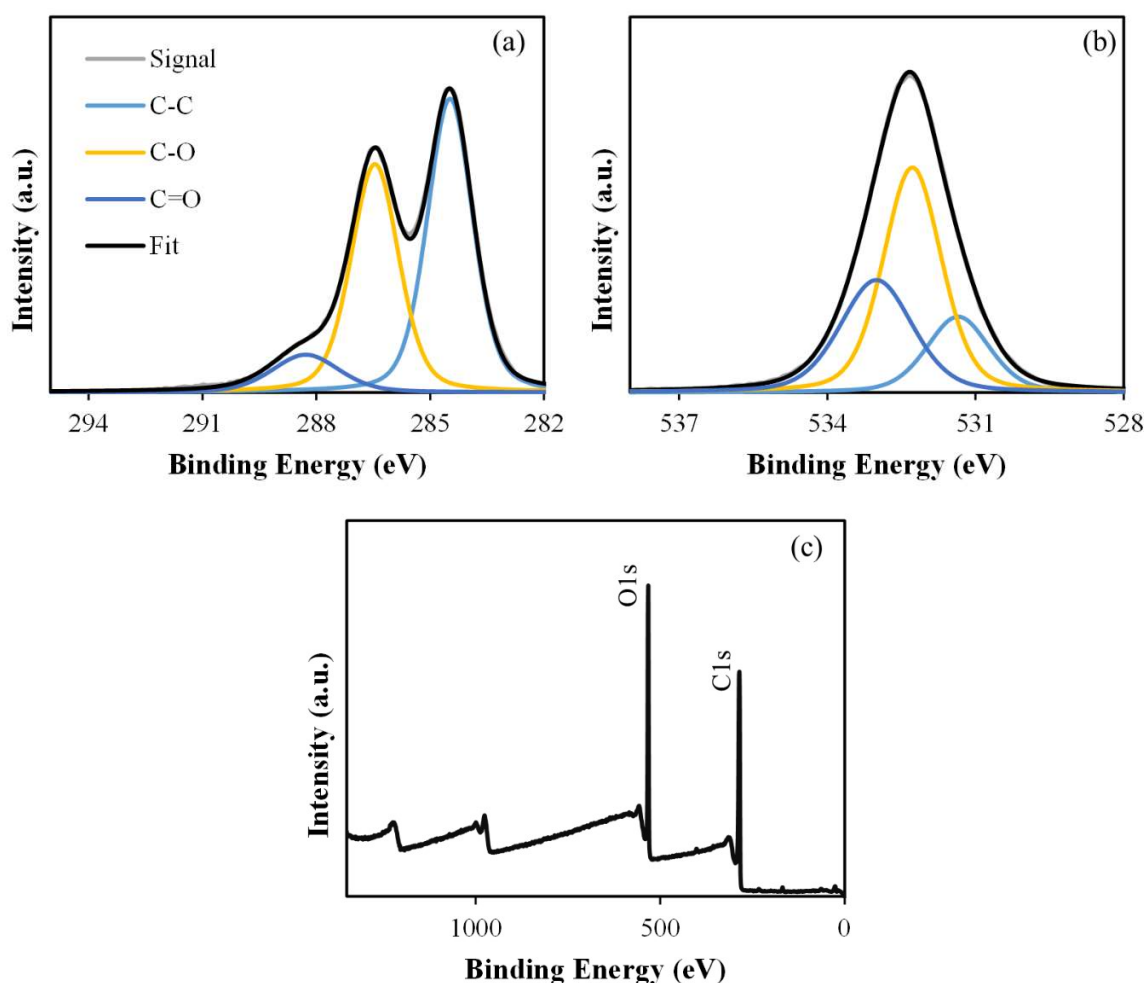


Figure 7: C1s (a), O1s (b), and survey (c) XPS spectrum of graphene oxide³³

Raman and ATR-IR spectra are given in Figure 8. Two broad peaks defining D, and G bands in the Raman spectrum at 1350, and 1585 cm^{-1} are deconvoluted to 5 peaks to understand the defect site ratios⁶⁸. These 5 peaks are D*, D, D'', G, and D' bands at 1100, 1350, 1500, 1580,

and 1610 cm^{-1} respectively. D*, D, D'', G, and D' bands are corresponding to disordered graphite, graphite defects, amorphous carbon, crystalline graphite, and phonons caused by defects respectively^{69–71}. Raman results demonstrate D band presence which cannot be observed in graphite⁷⁰. According to the D bands, during the oxidation of graphite defect sites are created. The ratios of the bands are given in Table 1.

Table 1: Signal ratios of D bands to G band of graphene oxide film⁶⁷

I_{D^*}/I_G	I_D/I_G	$I_{D''}/I_G$	$I_{D'}/I_G$
0.02	1.36	0.16	0.59

Broad signal peaks between 3000 , and 3500 cm^{-1} in the ATR-IR spectrum shown in Figure 8 (b) indicate the presence of water, and O-H bonds^{72–75}. This supports the results deduced from the XPS that the oxidation of the graphite is successful. Peaks at 1720 , 1420 , 1200 , and 1040 cm^{-1} correspond to carboxylic C=O stretching carboxylic O-H bending, hydroxyl C-O stretching, and epoxy C-O stretching respectively^{72–75}. Peaks at 1620 and 1580 cm^{-1} correspond C=C vibration and stretching, respectively⁷². The indication of C-O and C=O bonds also supports the success of the oxidation.

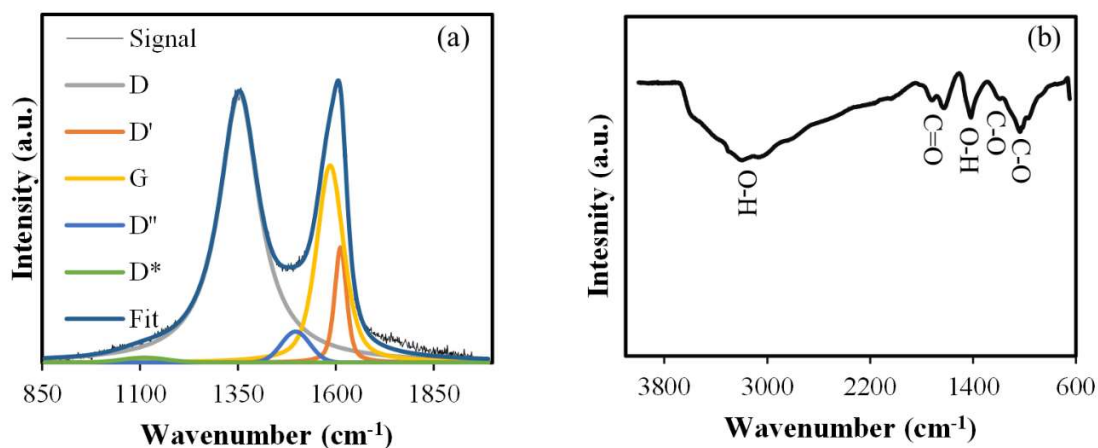


Figure 8: Raman (a), and ATR-IR (b) spectroscopies of graphene oxide film⁶⁷

In Figure 9 AFM imaging and height profiling of graphene oxide showed that the thickness of the sheets is 1.1 nm. This thickness proves the success of the exfoliation and sizes of the sheets. Evidence of oxidation of graphite in the graphene oxide film and solution is supported via XRD, XPS, AFM, and ATR-IR results.

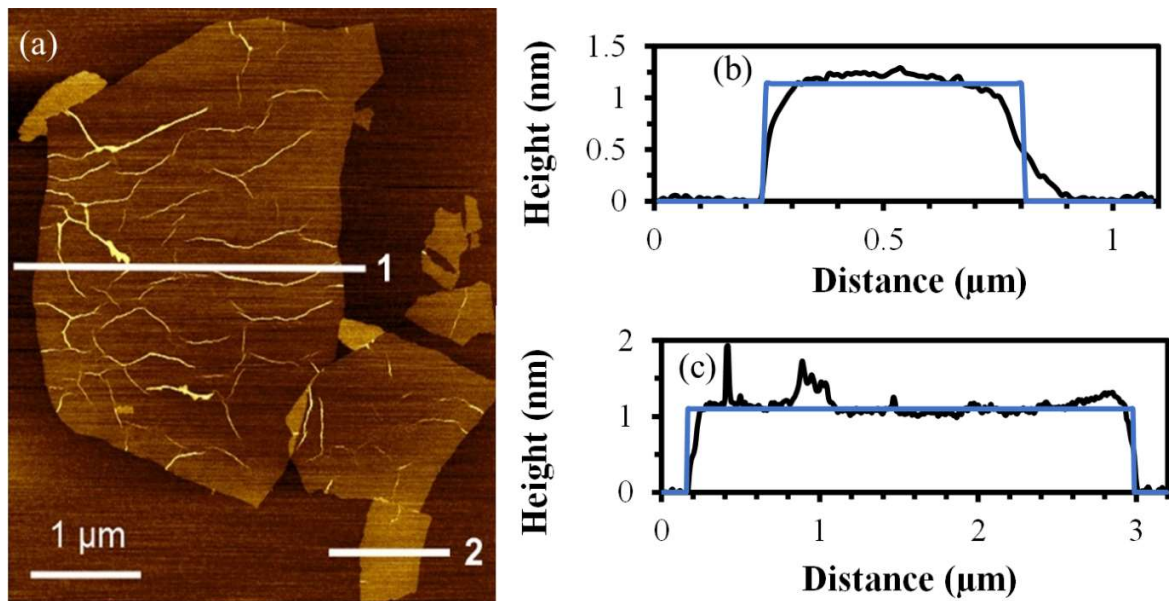


Figure 9: AFM image of graphene oxide (a), and height profiles of indicated lines (b), and (c)³³

2.3.2. Properties of Graphene Aerogels

During hydrothermal treatment of graphene oxide solution, partial reduction took place^{40,47}. As a result of the high number of oxygen-containing functional groups, attractions occur between the layers⁴⁷. These groups increase the π - π stacking between layers, which makes the random stacking⁴⁷. To investigate the reduction degrees, XRD, Raman, and XPS methods are used. As Figure 10 shows, the XRD pattern of graphene aerogel has a broad (002) plane peak at 23.8° ⁷⁶. Calculations with Bragg's equation indicates an interlayer distance of 0.371 nm. This value is 0.81 for graphene oxide film. Greater interlayer distance in graphene oxide is a consequence of oxygen-containing groups and intercalated water molecules. This decrease in the interlayer distance shows that reduction occurred to a considerable degree.

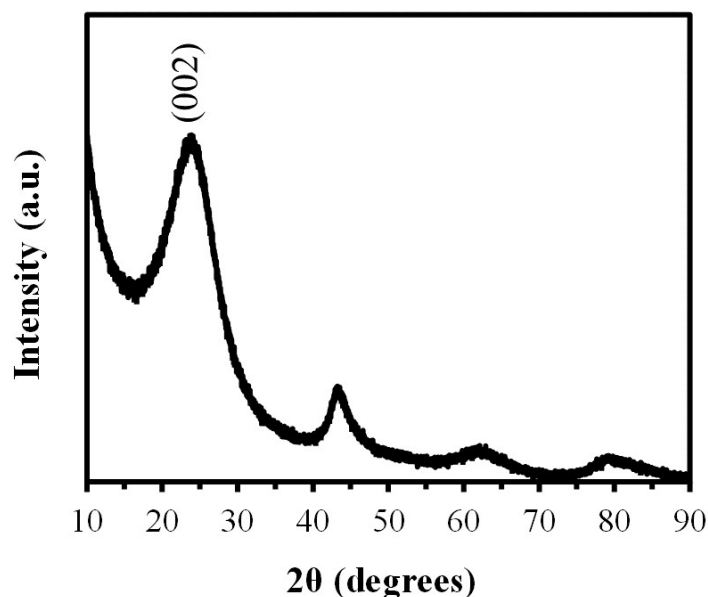


Figure 10: XRD pattern of graphene aerogel⁶⁷

For further understanding of the degree of reduction, the Raman spectrum of graphene aerogel, given in Figure 11 is deconvoluted to five peaks corresponding to D*, D, D'', G, and D' bands. D and G bands are demonstrating defects (diamond) and graphitic structure. Evidence shows that an increase in D band signals in Raman after reduction is recorded^{74,77}. As Table 2 demonstrates, I_D/I_G ratios increased compared to graphene oxide's Raman spectrum. The increase in these ratios shows an increase in defect sites. The partial reduction is also consistent with the literature in terms of the I_D/I_G ratio increase⁷⁴. It is recorded that thermal procedures and substrate addition on the graphene with 1 to 4 layer resulted in formation of D band⁷⁸. Similar effect from temperature may be the result of the D band in graphene aerogels. Also some of the defects occurred while synthesizing graphene oxide may also contributed the D band formation.

Table 2: Signal ratios of D bands to G band of graphene aerogel⁶⁷

I_{D^*}/I_G	I_D/I_G	$I_{D''}/I_G$	$I_{D'}/I_G$
0.12	1.68	0.32	0.66

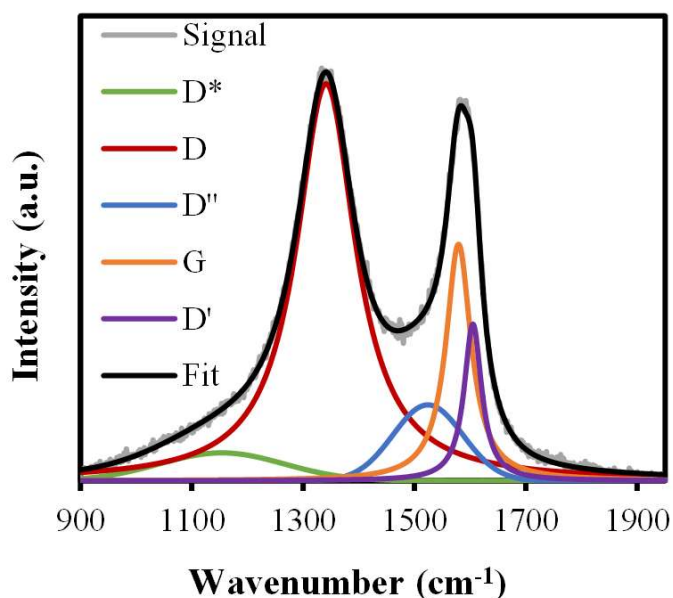


Figure 11: Raman spectrum of graphene aerogel³³

XPS is used to analyze the surface chemistry of the graphene aerogel. The spectrum deconvoluted to four peaks regarding graphene oxide with the addition of π - π^* transition at 291.1 eV. As mentioned before, XPS signal ratios of carbon-carbon bonds and carbon-oxygen are proportional to the actual carbon-oxygen ratio. In graphene oxide, carbon-oxygen single bonds and carbon-oxygen double bonds signals' ratio to carbon-carbon bonds' signals are 1.25, and 0.15 respectively. After the hydrothermal reaction, a resulting reduction can be exposed via a decrease of these ratios to 0.15, and 0.12. Carbon oxygen single, and double bonds in the graphene oxide are removed from the structure under heat and pressure.

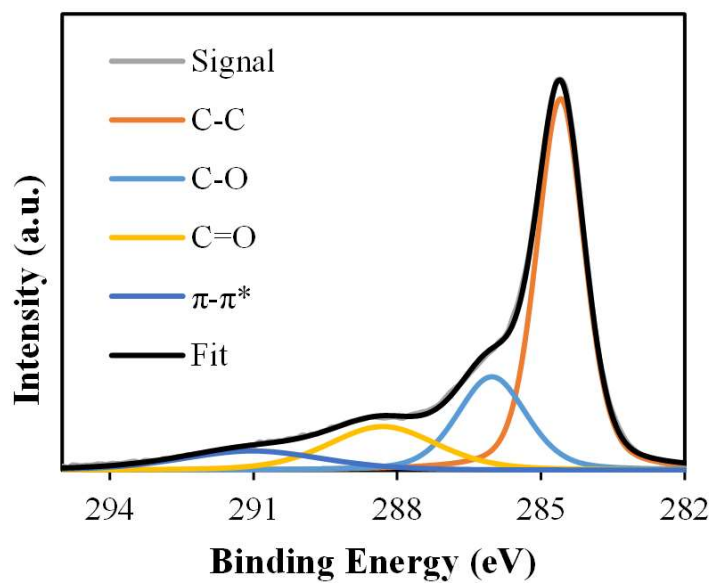


Figure 12: XPS C1s spectrum of graphene aerogel³³

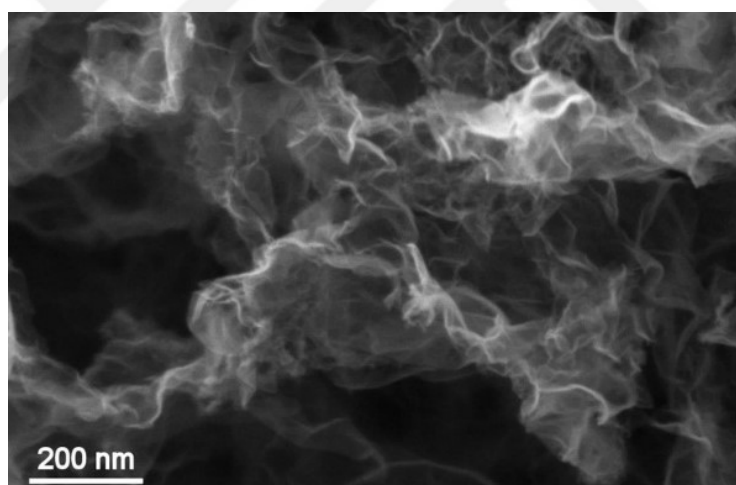


Figure 13: FESEM image of the graphene aerogel⁷⁹

In Figure 13, FESEM image of the graphene aerogel shows the porous structure. The surface area and pore sizes of the graphene aerogel is measured via nitrogen physisorption. According to the adsorption isotherm in Figure 14 (a), graphene aerogel's BET surface area is $708 \text{ m}^2 \text{ g}^{-1}$, the total pore volume is $1.54 \text{ cm}^3 \text{ g}^{-1}$, and micropore volume is $0.024 \text{ cm}^3 \text{ g}^{-1}$.

Pore distribution is given in Figure 14 (b), the figure shows the average pore diameter is 5.8 nm, while most of the pore diameters are smaller than 20 nm.

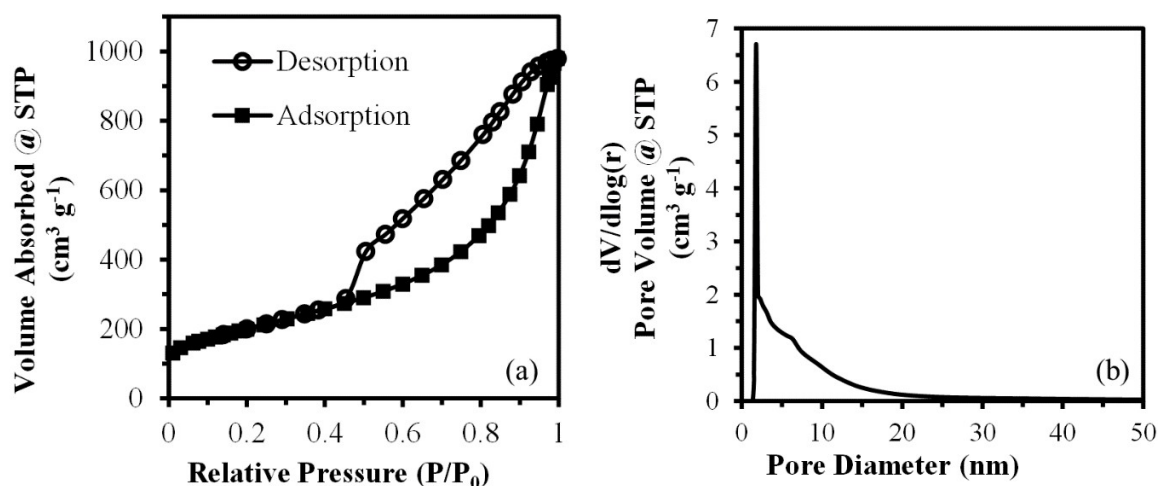


Figure 14: Nitrogen adsorption isotherm (a), and pore size distribution (b) of graphene aerogel⁷⁹

TGA is performed under nitrogen and dry air. The aim of heating samples under oxygen-containing and oxygen-free atmospheres is to determine their mass of solid residue and thermal stability, respectively. Samples are heated up to 800 °C with a 10 °C min⁻¹ ramp. Under nitrogen and high temperature, oxygen functional groups can be detached, which demonstrates the sample's durability against temperature. Under the oxygen-containing environment and high heat, carbon samples undergo a combustion reaction. In Figure 14 (a) aerogels undergo a combustion reaction with the presence of the oxygen. Products of this reaction are gaseous CO, and CO₂. Combustion resulted in no solid residue. With the help of this information, metal loaded samples' metal loading ratios can be found after they undergo the same procedure. In that case, a solid residue will remain. From the mass of residue mass of the metal can be calculated. In Figure 14 (b) 27% mass loss can be observed under an oxygen-free environment. This mass loss is occurred because of the removal of the oxygen-

containing groups in the high temperatures⁸⁰. The relation between XPS and mass loss in TGA is calculated via following equation:

$$O(w/w)\% = \frac{\left(\frac{I_{C-O} + I_{C=O}}{I_{C-O} + I_{C=O} + I_{C-C/C=C}} \right) \times Mw(O)}{\left(\frac{I_{C-O} + I_{C=O}}{I_{C-O} + I_{C=O} + I_{C-C/C=C}} \right) \times Mw(O) + \left(\frac{I_{C-C/C=C}}{I_{C-O} + I_{C=O} + I_{C-C/C=C}} \right) \times Mw(C)}$$

In this equation, I corresponds to the XPS peak area of the subscripted bond, Mw corresponds to the molecular weight and O (w/w) % corresponds to the weight percent of the oxygen in aerogel. When this equation is applied for XPS spectra of graphene aerogel, it is found that 26.5% of aerogels are oxygen by mass. When TGA is performed, oxygen on the graphene aerogels are removed and resulted in a 27% mass loss. Even though XPS is a surface analysis method and TGA is a bulk analysis, the oxygen mass observed in both studies are supporting each other.

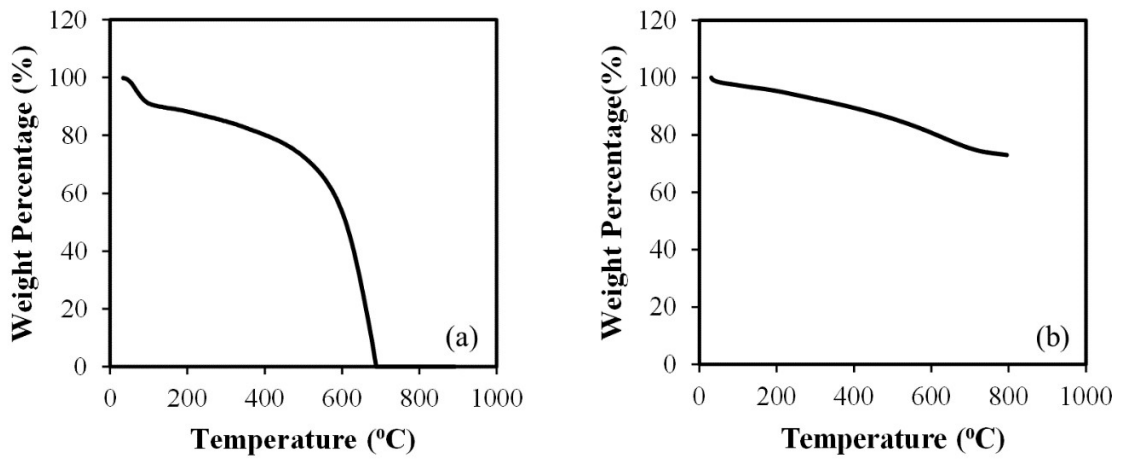


Figure 15: TGA graphs of graphene aerogel under dry air (a), and nitrogen (b)⁶⁷

2.4.Conclusion

In this chapter, graphene oxide is synthesized from graphite via modified Hummers' method. Graphite's oxidation is confirmed via AFM, XRD, XPS, and ATR-IR methods. Morphology is investigated under FESEM. Graphene hydrogels are synthesized with hydrothermal reaction. During the reaction, a partial reduction has also occurred. The partial reduction is verified via XRD, XPS, and Raman. The 3D structure's properties such as surface area and pore sizes are measured with BET. A surface area of $708 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $1.54 \text{ cm}^3 \text{ g}^{-1}$, and a micropore volume of $0.024 \text{ cm}^3 \text{ g}^{-1}$ are measured. For a catalyst support increase in the surface area also increase in the exposed active sites which eventually increase the catalytic activity.

Chapter 3: Iron Loaded Graphene Aerogels as a Catalyst for Ammonia

Decomposition Reaction

3.1.Introduction

Because of the harmful nature, and limited supply of fossil fuels, the utilization of new sources of sustainable energy is important. With using clean energy, the prevention of global warming is necessary because of the global impact of CO₂ emitted from fossil fuel consumption¹. With today's technology, the reduction of CO₂ is a very expensive procedure to be sustainable⁸¹. Instead, lowering the emission of CO₂ may be a more sustainable method for the recession of global warming. During the ongoing Covid-19 pandemic, countries established lockdowns⁸². During these lockdowns, a decrease in emission and concentration of CO₂ in the atmosphere is observed due to a decrease in energy demand⁸². These hard times showed that, if the hydrogen economy partially or fully adapted to daily life, the negative effects of CO₂ may shrink every year. To adopt the hydrogen economy, production, storage, and transportation of hydrogen must be efficient and safe. To design energy-efficient, alternative fuels, functioning catalysts are essential. For instance, ammonia decomposition reaction yields hydrogen which can be used as a fuel. Both production and usage of hydrogen do not generate greenhouse gases which are in gaseous form. However, the decomposition reaction of ammonia requires high temperatures, even with catalysts². Ruthenium showed high ammonia conversion rates at low temperatures with carbon support materials². Because of ruthenium's lack of availability and high prices, less valuable, and more abundant transition metal alternatives drew attention². The use of nickel, cobalt, and iron catalysts for the ammonia decomposition reaction took the interest of many researchers. These metals are used on different support materials to increase the surface area to compete with already

proved ruthenium's high ammonia decomposition ability. In ammonia decomposition reaction various support materials are used to enhance the performance of iron catalysts. Carbon nanotubes, porous silica, and other high surface area supports are used^{22,23,61,83}. Graphene aerogel is never used as a support material of iron catalyst for ammonia decomposition reaction. The definition of an efficient catalyst by Yin et al. consists of three main properties, stability in reaction conditions, high surface area, and electrical conductivity¹⁹. Graphene aerogels satisfy all of these criteria. In this chapter, ammonia decomposition performances of iron-loaded graphene aerogels are investigated to compete with other catalysts in the literature contain more active metals. Addition to iron loaded graphene aerogels' ammonia decomposition performance evaluations, alkali metal added iron loaded graphene aerogels' ammonia decomposition are measured. In some studies, the addition of smaller metals increased catalytic performance. The effect of the smaller metals is the prevention of the sintering of the active metals, however, in ammonia decomposition literature inconsistency is present for the effect of the smaller metals¹⁹. Alkali metal addition to transition metal catalysts for other reactions helped increasing catalyst's activity^{84,85}. Contrary to this, some studies show alkali metal addition may have a negative effect on catalytic activity⁸⁵. In this chapter, iron particles are loaded on high surface area graphene aerogel to measure catalytic activity for ammonia decomposition reaction. Also, in order to display the effects of the alkali metals as additives, lithium, sodium, and potassium additions are made and measured for catalytic activity.

3.2. Materials, and Procedure

3.2.1. Materials

99.9995% graphite produced by Alfa Aesar is used as a precursor. For the oxidation of graphite, NaNO_3 from Alfa Aesar, KMnO_4 , and H_2O_2 (30%) from Merck Millipore, HCl (37%), and H_2SO_4 (95-97%) from Sigma Aldrich are obtained. For solvent exchange 99% ethanol from Isolab. For the metal loadings, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.0-101.0%) from Alfa Aesar is used. NaCl and KCl purchased from Merck Millipore, LiCl purchased from Sigma Aldrich. In all the procedures distilled water with 18.2 M Ω electrical resistance is used.

3.2.2. Graphene Oxide

Graphene oxide solution is used in this chapter to synthesize aerogels. Details of graphene oxide synthesis are given in Section 2.2.2.

3.2.3. Graphene Aerogel

Graphene alcogels are used in this chapter to load metals by impregnation. Details of graphene aerogel synthesis are given in Section 2.2.3.

3.2.4. Iron Loading on Graphene Aerogels

Metals are loaded via the impregnation method in the impregnation solution. Impregnation solutions are prepared with ethanol and precursor iron salt. After solvent exchange alcogels are dipped in the impregnation solution. The precursor used in this work is $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. A gradient of impregnation solutions is used to control the metal loading ratio. A gradient of concentrations of 0.1, 0.06, 0.03, 0.015, and 0.0077 M are used for the iron-loaded catalysts. Alkogels stayed 24h in precursor solutions to complete metal loading. After the metal loading, alcogels are dried via the aforementioned supercritical drying. Alkogels are placed in a steel vessel filled with ethanol. From this vessel, CO_2 flowed at 60 °C under 120 bar

pressure. In this temperature, and pressure CO₂ is in the supercritical phase which can dissolve ethanol. Without collapsing the pores of aerogels drying is taken place. After 2h of CO₂ flow, ethanol in pores is completely removed. Finally, the thermal reduction is applied to remove remaining carbon-oxygen bonds and iron particles. During the thermal reduction, it is expected that nitrate ions bound to iron are removed and iron particles reduced to the metallic state. Thermal reduction for iron-loaded aerogels is conducted at 700 °C. The thermal reduction is conducted with a degasification step at 110 °C under pure Ar. After degasification under reducing gas mixture (10% H₂, 90% Ar) temperature increased to 700 °C, and under the same atmosphere, reduction continued for 2 hours at 700 °C.

3.2.5. Alkali Metal Addition on Iron Loaded Graphene Aerogels

Alkali metal addition is made via alkali metal salt addition to 0.0077 M Fe(NO₃)₃·9H₂O impregnation solution. Alkali metal salt concentrations are 2.0mM in the impregnation solution. Alkali metal salts used are LiCl, NaCl, and KCl. Drying, and thermal reduction conditions are as described in 3.2.4.

3.2.6. Characterization of Metal Loaded Graphene Aerogels

Iron loadings are determined via TGA under dry air. At 800 °C, and in the presence of oxygen, carbon support completely burns. Remaining iron oxide is determined via XRD. By the mass of remaining metal oxide, initial mass, and mass percentage of the loaded iron ratio can be calculated. For the catalysts, XRD is used to determine the loaded metals' state, it is expected to be in the metallic state. Surface chemistry is investigated with XPS. Raman is used for the investigation of defects. Morphology is investigated under SEM to understand the changes between aerogels after metal loading. These characterization methods are applied

to alkali metal added catalysts either. The objective is to understand the changes between alkali metal added and only iron loaded aerogels.

3.2.7. Catalytic Performance Measurements of Iron Loaded Graphene Aerogels

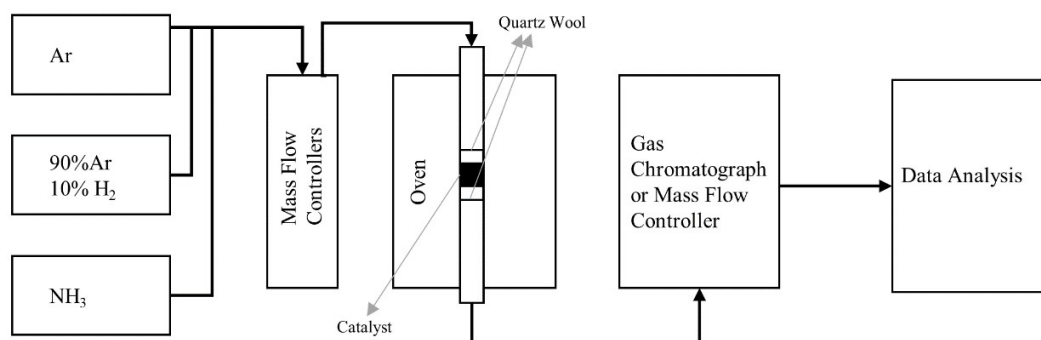


Figure 16: Diagram of catalytic performance measurement setup

Catalytic performance measurements are made via Agilent Technologies 7820A Gas Chromatograph (GC) is used with HP/Plot-Q column and Thermal Conductivity Detector (TCD) detector and Alicat mass flow controller. Iron loaded graphene aerogels are placed in a quartz tube stabilized with quartz wool as the diagram in Figure 16 shows. In situ thermal reduction is carried out in the reaction system before data collection. Data collection is done under pure NH_3 flow. A gradient of reaction temperatures and a gradient of space velocity of NH_3 is used in data collection. Temperature gradient used is 450, 500, 550, and 600 °C whereas space velocity gradient is 9000, 22500, 45000, 90000, and 180000 $\text{mL NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$. For every reaction temperature, ammonia conversion data are collected for every space velocity in the gradient. Conversion data are calculated from NH_3 area measured by GC or flow rate measured by MFC according to the suitable calibration curve.

GC is a device that can separate the analytes without identifying them. To identify the compounds from GC's results, a calibration is necessary. In this study, GC column could

separate H₂ and N₂ mixture from NH₃. To be able to calculate the NH₃ composition in an NH₃, H₂, and N₂ mixture, a calibration curve is needed. To construct the calibration curve, known amounts of NH₃, H₂, and N₂ mixture are analyzed with GC. Every mixture is associated with a conversion rate according to the ammonia decomposition reaction's stoichiometry. From this calibration, four linear curves are drawn and presented in Figure 17. Each of the curves is accurate in a different range of conversion. These ranges are 0-10%, 11-50%, 51-90%, and 91-100% ammonia conversion.

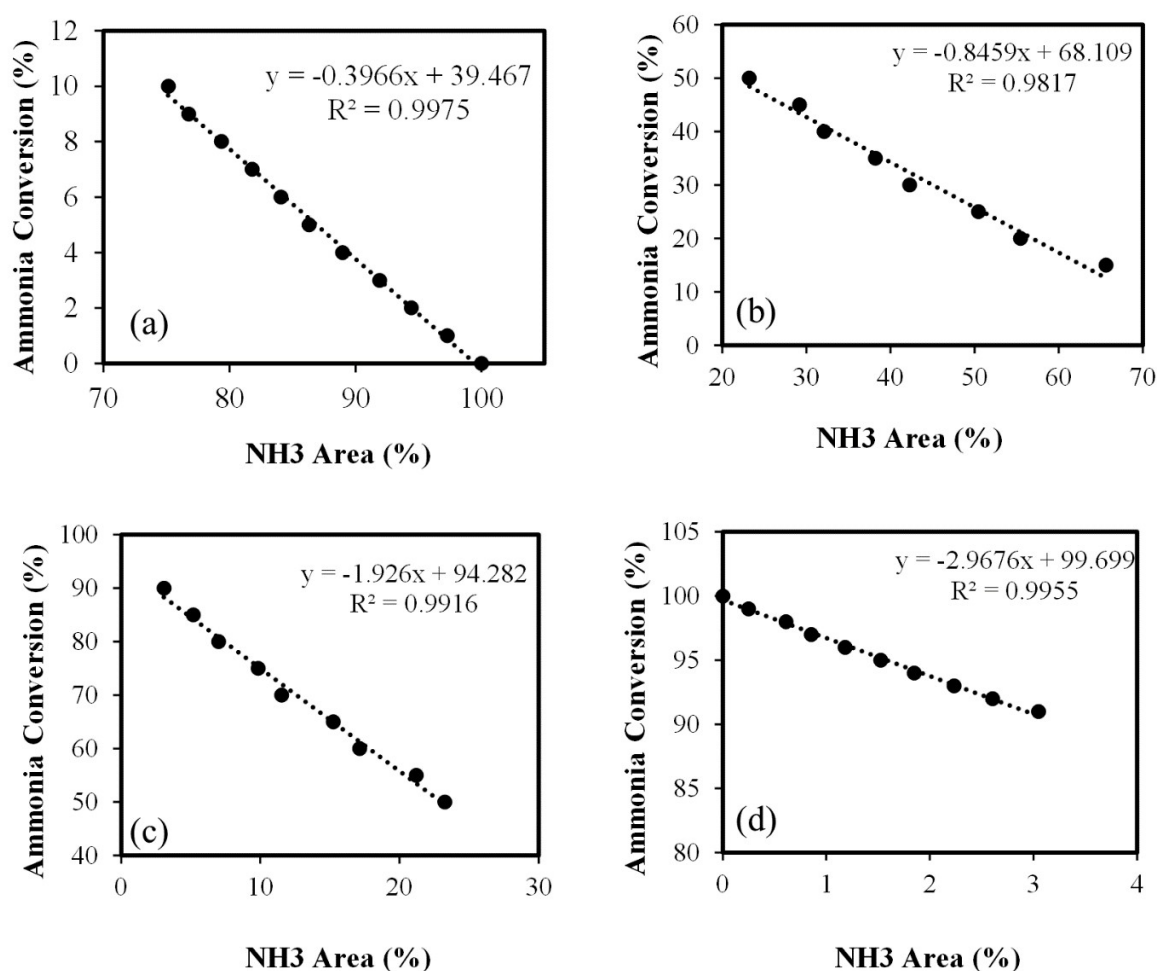


Figure 17: Calibration curves of GC separated in regions according to ammonia conversion. 0-10% (a), 11-50% (b), 51-90% (c), and 91-100% (d)

MFC is a device which neither separates nor identifies the analytes, it only controls and displays the flow gases. However, when a lower rate of flow is fed to an MFC with a higher set point, MFC displays the actual flow. MFC displays the flow according to a built-in calibration for a specific gas or mixtures. When the MFC is set to a specific gas, but the feed is a mixture, the device cannot display the correct flow. MFC calibration is carried out via feeding the known concentrations of NH_3 , H_2 , and N_2 mixture. The flow rate obtained from MFC are collected and every flow rate is associated with the different conversion rate. In Figure 18 calibration curves of MFC are given. From these graphs, it is deduced that even the initial flow of ammonia changes, the relationship between displayed flow and ammonia conversion is linear. In other words, regardless of the flow rate of the reaction, ammonia conversion rate can be calculated from the value MFC displays. For all calibrations, setup given in Figure 16 is installed without a catalyst.

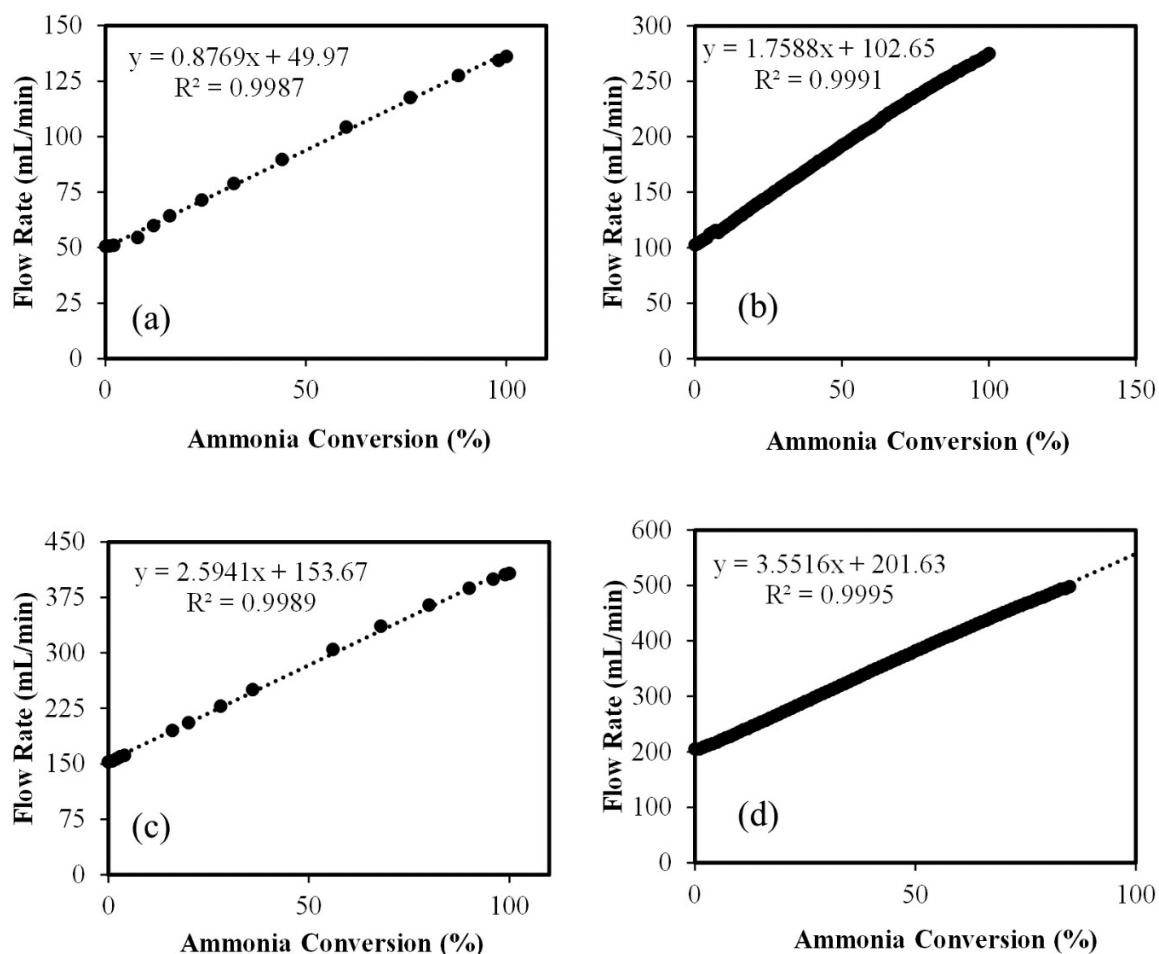


Figure 18: MFC calibration curves for 50 (a), 100 (b), 150 (c), and 200 (d) ml/min flow rates

3.3. Results, and Discussion

3.3.1. Properties of the Iron Loaded Graphene Aerogels

Iron loaded aerogels' metal loadings can be quantified via TGA. TGA is performed under dry air, samples heated up to 800 °C with a 10 °C per minute ramp. In the presence of the oxygen, graphene is converted into CO and CO₂. In 2.3.2 it is proven that graphene aerogels do not leave any solid residue that contributes to the final mass of metal oxide. TGA results are given in Figure 19. From the remaining metal oxide mass, the initial iron mass can be calculated. To make this back-calculation the iron oxygen ratio of the metal oxide must be

known. To determine the metal oxide, XRD is used. In Figure 20 XRD pattern of the remaining metal oxide is compared with the literature, and matched with Fe_2O_3 . Peaks at $2\theta = 33.3, 35.8, 41.1, 49.8, 54.5, 57.8, 62.8,$ and 64.4 degrees are matched with Fe_2O_3 (JCPDS No: 01-072-6226)⁸⁶. Initial iron mass is calculated from the final mass of Fe_2O_3 . In Figure 21 iron-loaded graphene aerogels' XRD pattern is given. The iron particles are compared with the database. Peaks are matched with metallic iron, also matching peaks with natural oxide of iron FeO is found. Iron oxide is found on the aerogels because of the exposure to oxygen. In the performance measurements in situ reduction is preferred to prevent iron oxide formation. In the XRD pattern peaks at $2\theta = 44.6,$ and 65.0 degrees are matched with metallic iron (JCPDS No: 06-0696)⁸⁷. Peaks at $2\theta = 36.5, 42.1,$ and 60.5 degrees are matched with FeO (JCPDS No: 01-089-2468)⁸⁸. The broad peak at $2\theta = 26$ degrees is matched with graphene aerogel. Average crystal sizes are calculated via Scherrer equation⁶⁴:

$$D_{hk} = \frac{H \times \lambda}{\beta_{hkl} \times \theta}$$

Scherrer equation is applied to the peaks at $2\theta = 44.6$ degrees which is the most intense peak of iron. At $2\theta = 43.3$ degrees another peak is present. To eliminate the error the peak of iron is fitted before calculations.

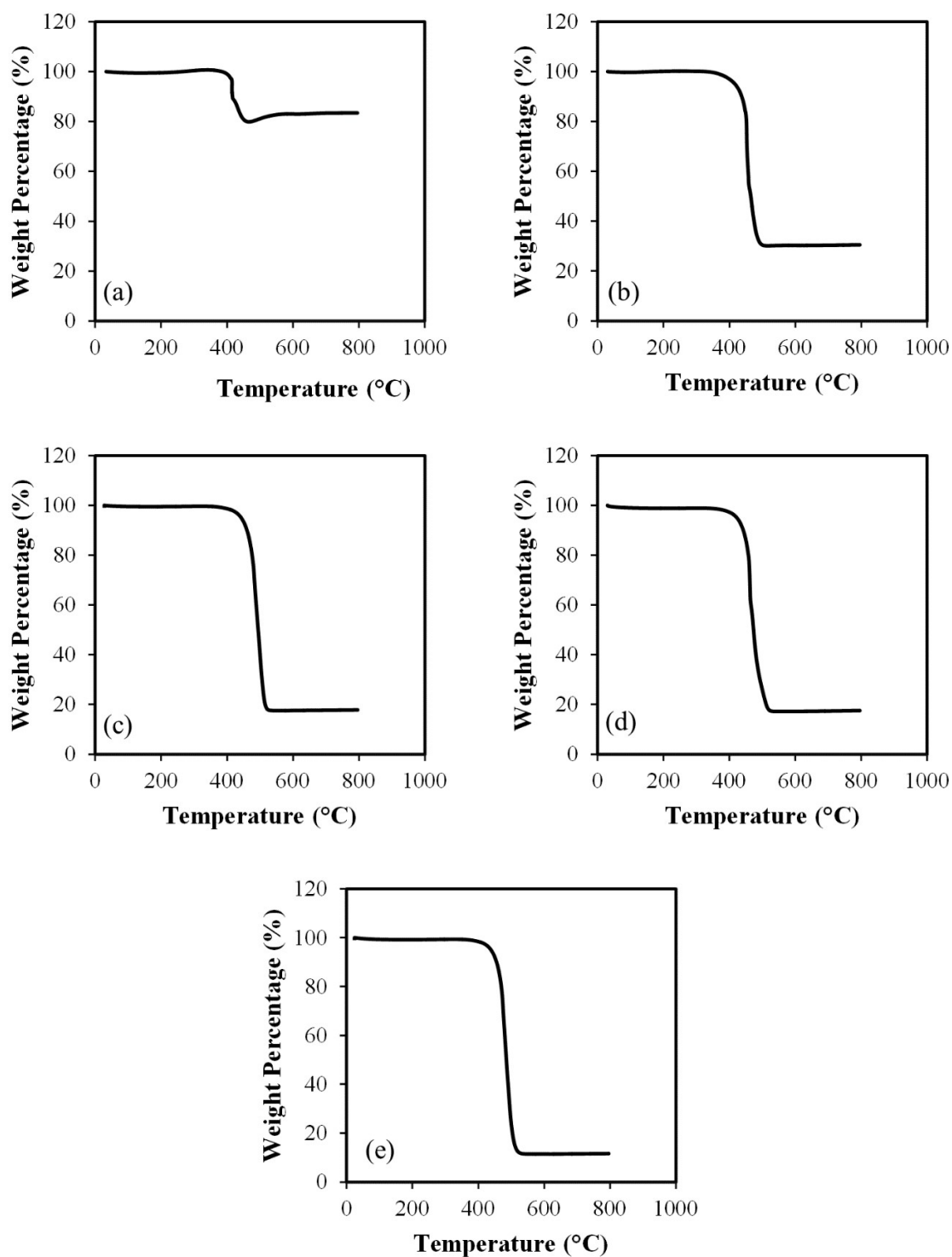


Figure 19: TGA graphs of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

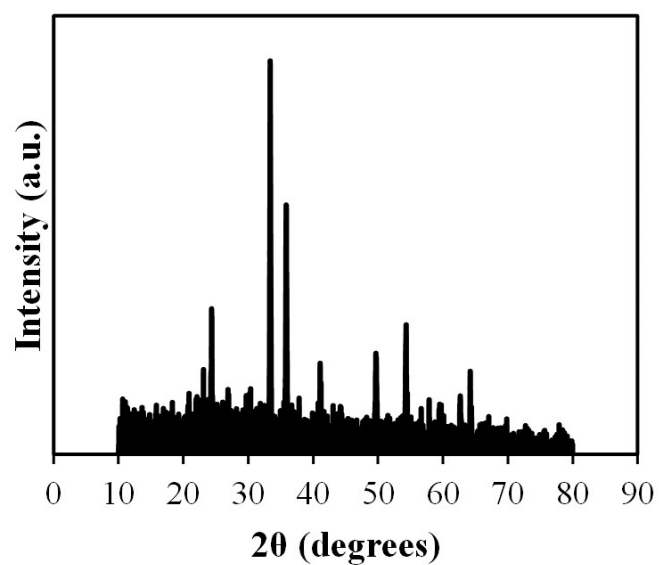


Figure 20: XRD pattern of the remaining metal oxide from TGA

Table 3: Iron loading ratios according to the samples' impregnation solution concentration, and average crystal size of iron according to Scherrer Equation

Impregnation Solution Concentration (mol/L)	Mass Percentage of Iron Oxide (Fe₂O₃) (%)	Mass Percentage of Iron (%)	Average Iron Crystal Size (nm)
0.0077	11.62	8.12	39.48
0.015	17.53	12.26	43.07
0.03	17.80	12.44	36.45
0.06	30.51	21.33	39.47
0.1	83.42	58.34	56.84

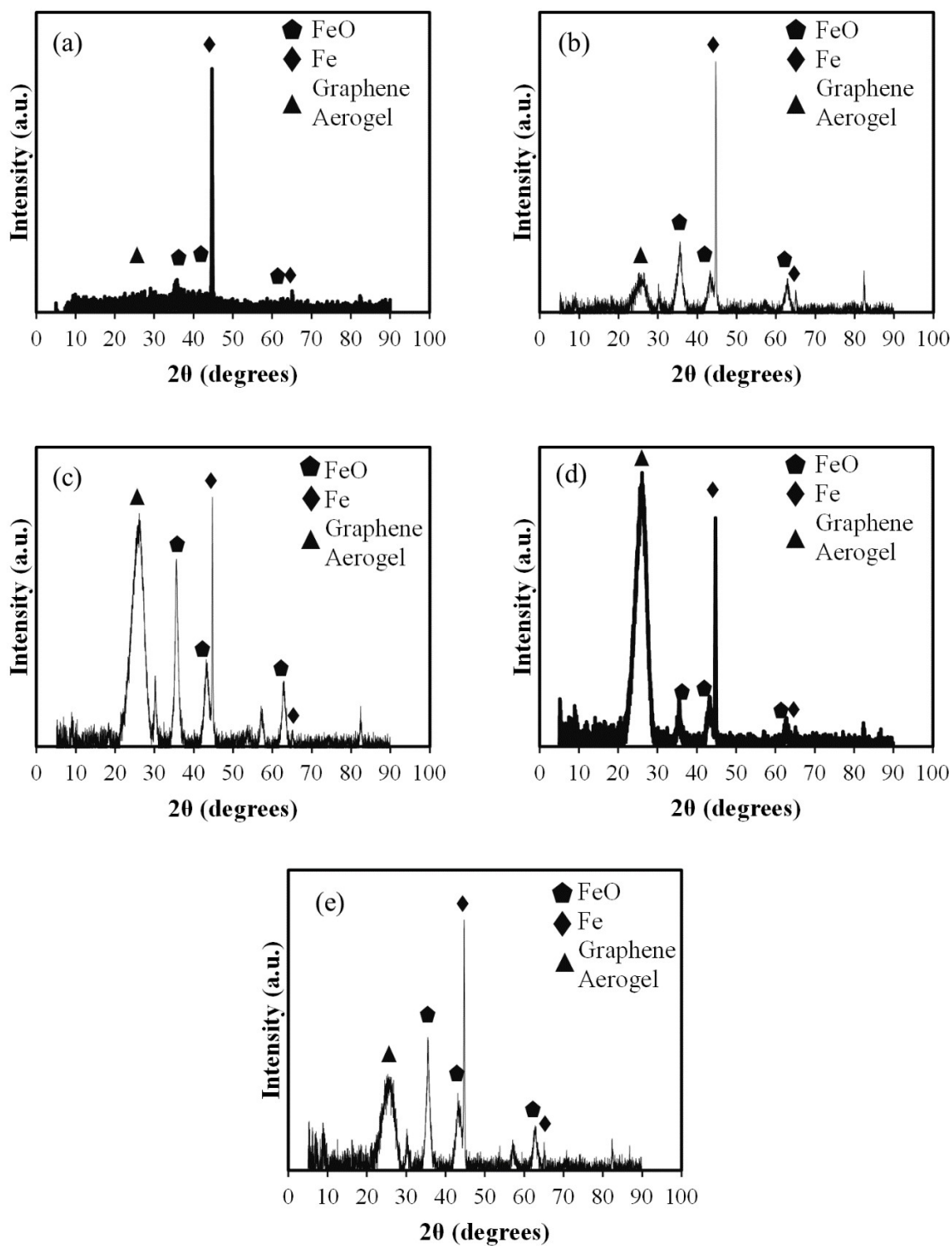


Figure 21: XRD patterns of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

To reveal the amount of the reduction and state of the iron particles, XPS C1s and Fe2p_{3/2} spectra are investigated. In Figure 22 XPS spectra of iron-loaded graphene aerogel are given. C1s spectrum is deconvoluted to 4 peaks similar to graphene aerogel's C1s spectrum. Peaks at 284.5, 286.5, and 288.0 eV are matched with carbon-carbon double, and single bonds, carbon-oxygen single bonds, and carbon-oxygen double bonds respectively⁶⁶. The fourth peak at 291.1 eV corresponds to the π - π^* transition. Fe2p_{3/2} spectrum is deconvoluted to three peaks at 710.8, 714.6, and 719.4 eV. XPS peak of metallic iron is at 707 eV⁸⁹. The metallic iron that is observed in XRD, cannot be seen in the XPS. These peaks are matching with Fe₂O₃, which is not present in the catalyst according to the XRD pattern⁹⁰. The reason is, under high energy X-ray, iron oxidizes³³. In XPS, not detecting the metallic form of the iron is not decisive about the form.

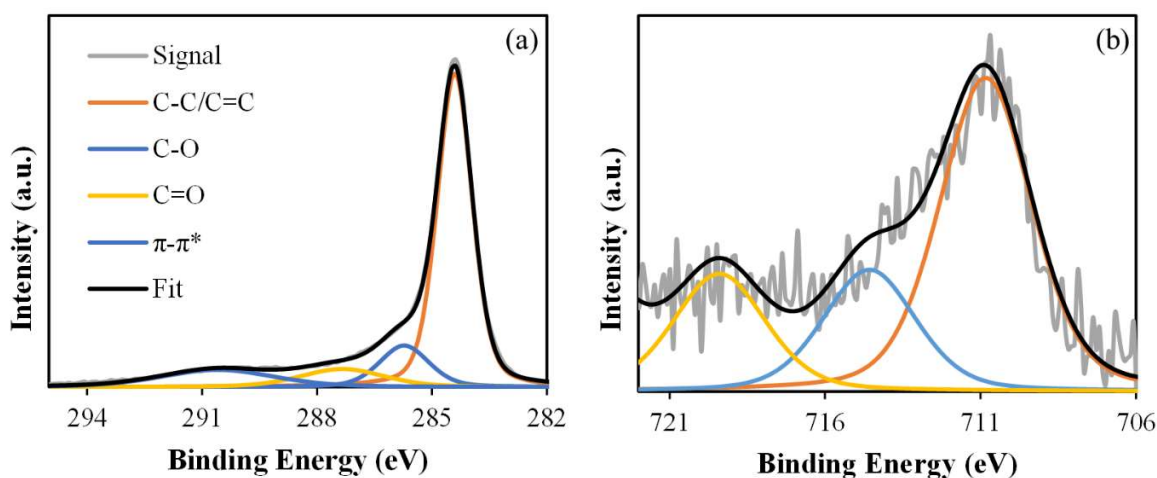


Figure 22: XPS C1s (a), and Fe2p_{3/2} (b) spectra of 12.44% iron-loaded graphene aerogel after thermal reduction

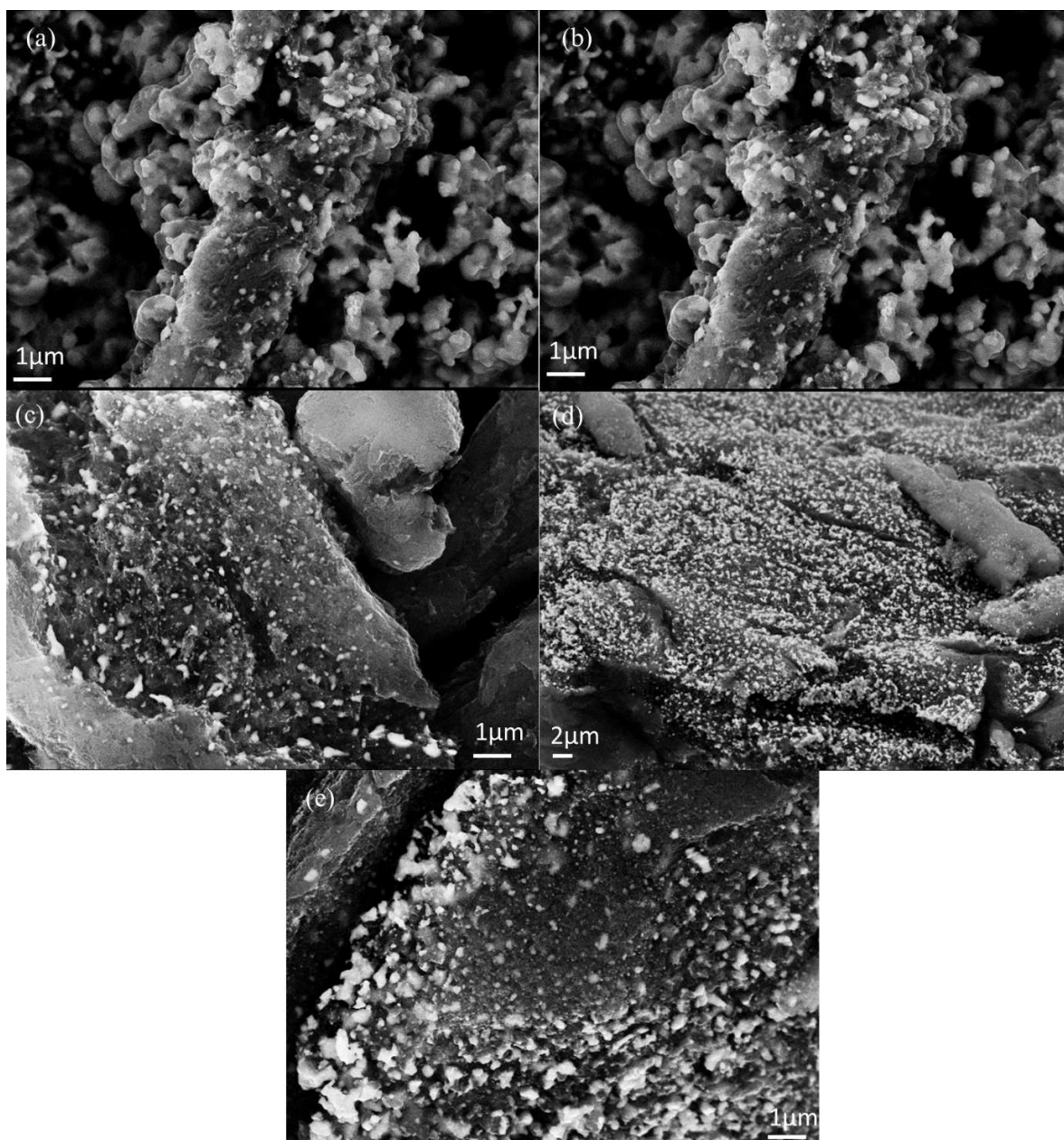


Figure 23: SEM images of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

In Figure 23 SEM images are given. Imaging shows the dispersion of the iron particles on the graphene aerogel. The porous structure is protected during the metal loading procedure. Defect ratios are determined via Raman spectroscopy. I_D/I_G ratios are given in Table 4. Impregnation solution concentration does not affect the defect amounts, that can be deducted

from the I_D/I_G ratios calculated from Raman spectra. D band represents the defects of the support material. According to the ratios, metal loading did not affect the defect amounts.



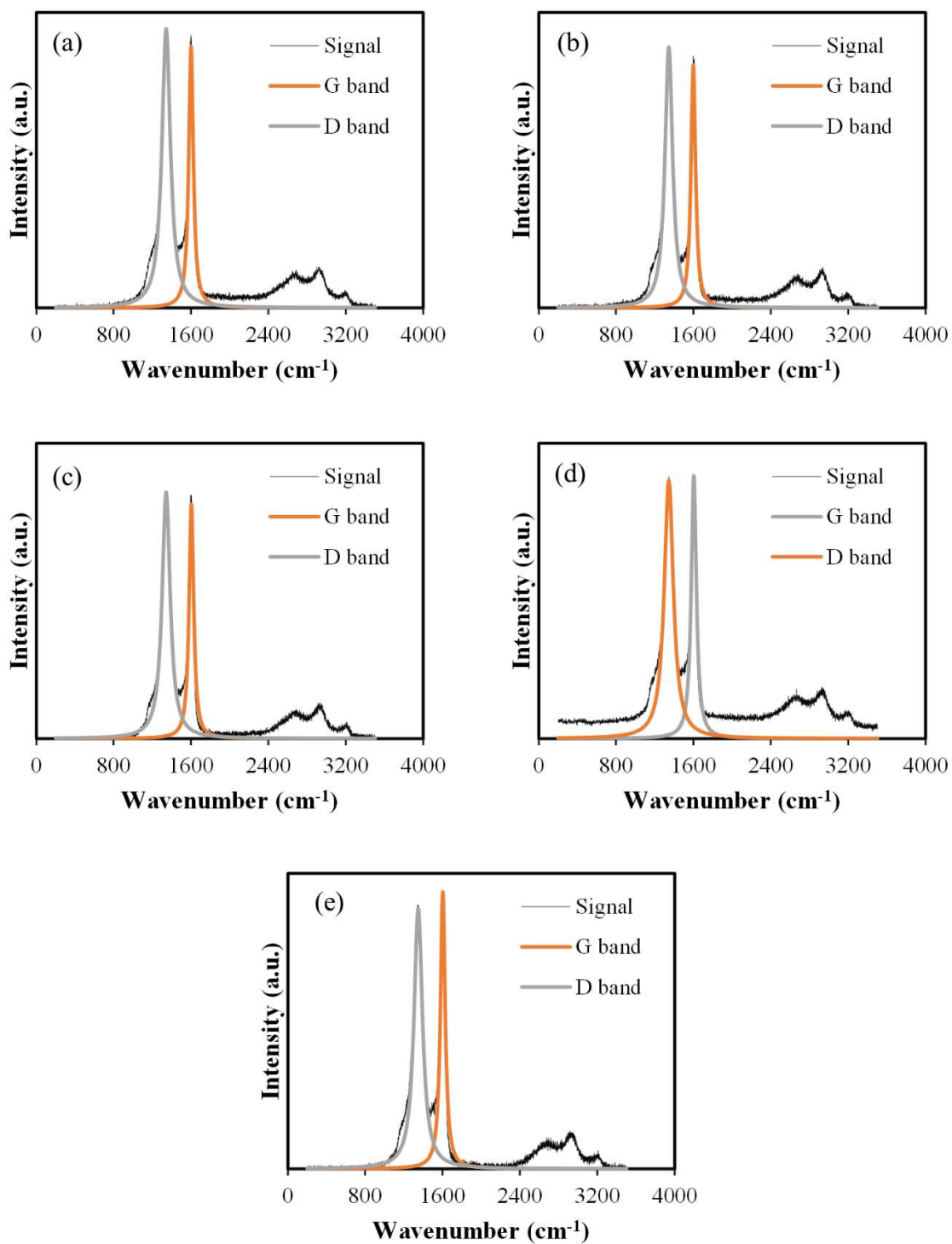


Figure 24: Raman spectra of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

Table 4: I_D/I_G ratios of iron-loaded graphene aerogels

Impregnation Solution Concentration (mol/L)	Mass Percentage of iron (%)	I_D/I_G
0.0077	8.12	0.96
0.015	12.26	0.99
0.03	12.44	1.01
0.06	21.33	1.03
0.1	58.34	1.03

3.3.2. Properties of Alkali Metal Added Iron Loaded Graphene Aerogels

Alkali metal added iron-loaded aerogels' metal loadings can be quantified via TGA. TGA is performed under dry air, samples heated up to 800 °C with a 10 °C per minute ramp. In the presence of the oxygen, graphene is converted into CO and CO₂. In 2.3.2 it is proven that graphene aerogels do not leave any solid residue that contributes to the final mass of metal oxide. TGA results of alkali metal added iron-loaded graphene aerogels are presented in Figure 25. The iron amount in the samples is calculated via back-calculation from the remaining metal oxide mass. In Figure 20 XRD pattern of the remaining metal oxide is compared with the literature, and matched with Fe₂O₃. Figure 26 presents the XRD patterns of the alkali metal added samples. As the only iron-containing samples alkali metal added samples' XRD peaks are matched with metallic iron, FeO, and graphene aerogel. In XRD patterns no peaks corresponding lithium, sodium, or potassium were found. This may be caused by the amount of the alkali metals compared with the iron amount. From the XRD

patterns, average crystal sizes are calculated via the Scherrer equation. Iron loading amounts and average crystal size of iron are presented in Table 5.

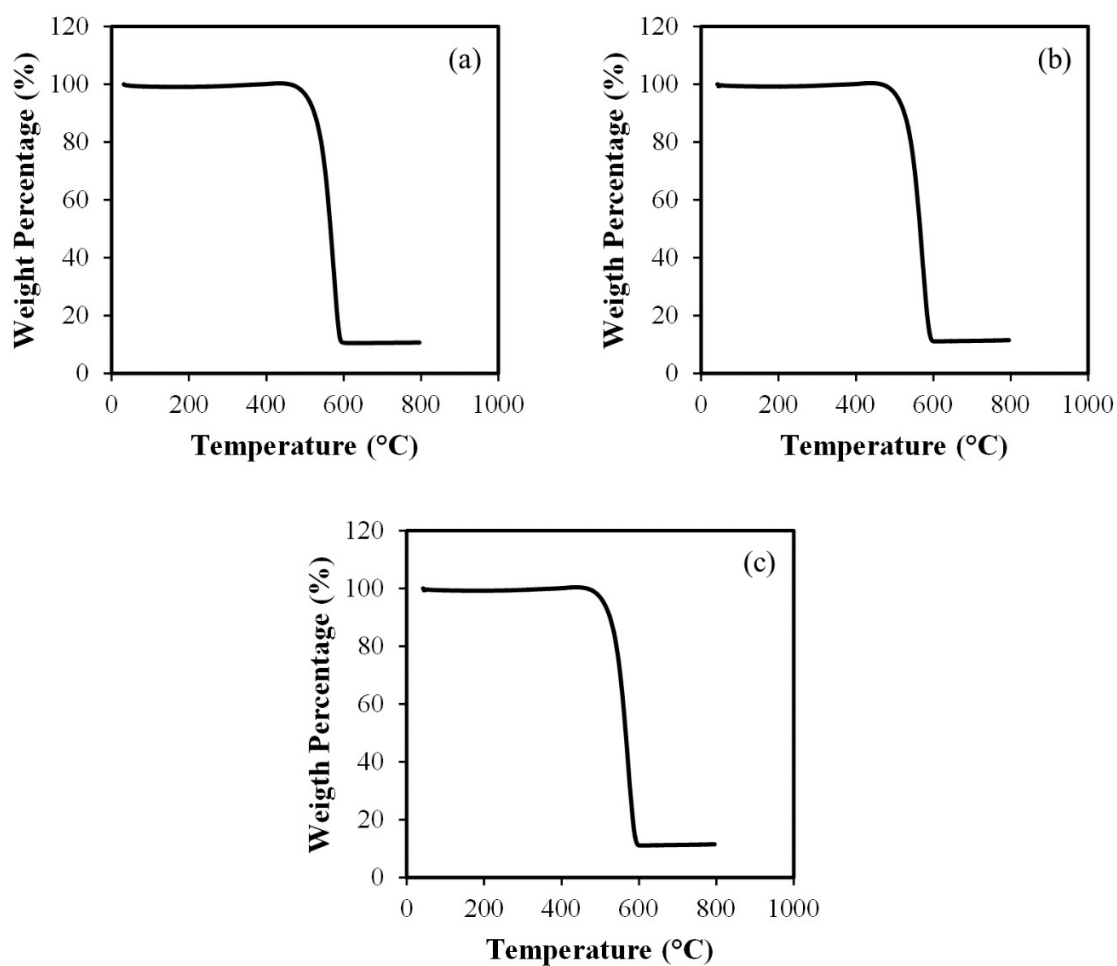


Figure 25: TGA graphs of lithium (a), sodium (b), and potassium (c) added iron-loaded graphene aerogels

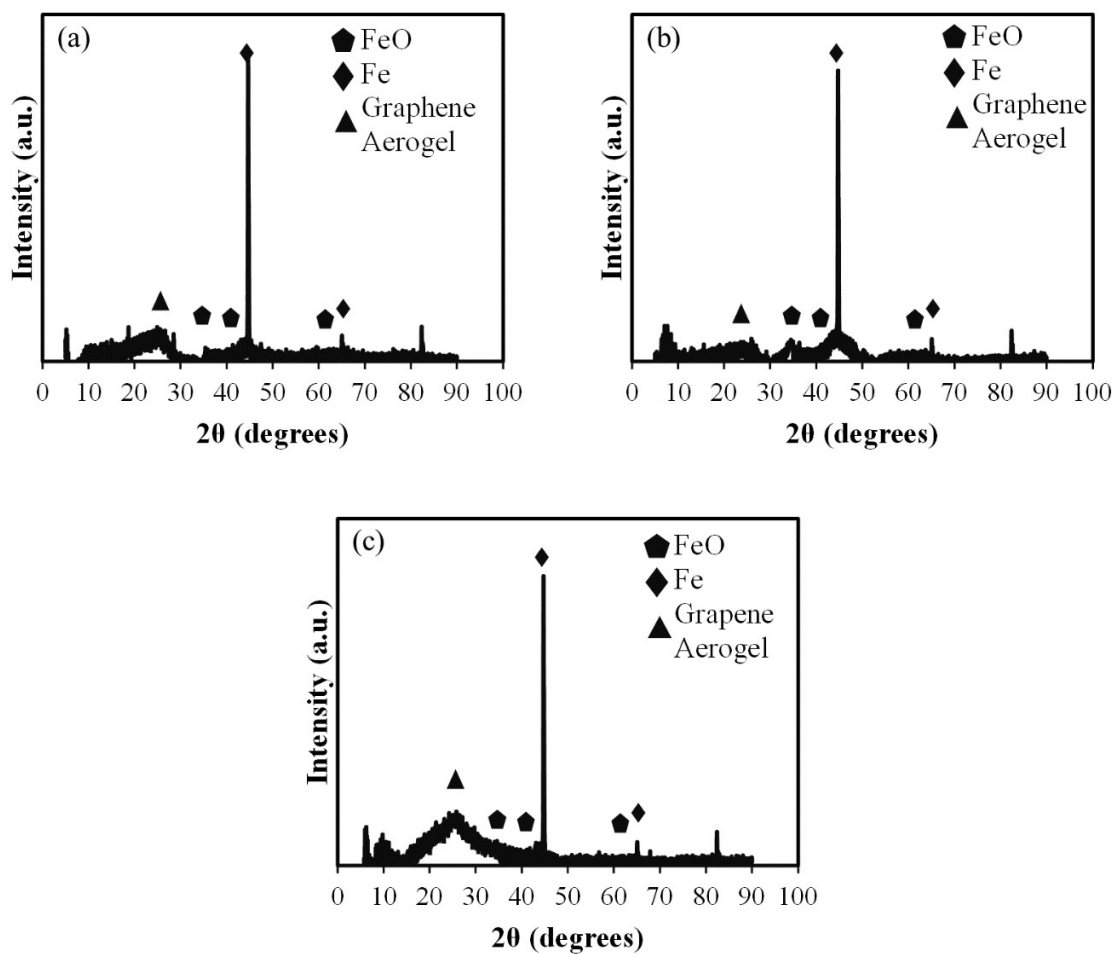


Figure 26: XRD patterns of lithium (a), sodium (b), and potassium (c) added iron-loaded graphene aerogels

Table 5: Iron loading ratios according to the samples' impregnation solution concentration, and average crystal size of iron according to Scherrer Equation

Impregnation Solution Concentration (mol/L)	Alkali Metal, and Impregnation Solution Concentration (mmol/L)	Mass Percentage of Iron Oxide (Fe ₂ O ₃) (%)	Mass Percentage of Iron (%)	Average Iron Crystal Size (nm)
0.0077	K, 2.0	12.25	8.56	54.66
0.0077	Na, 2.0	11.47	8.02	50.74
0.0077	Li, 2.0	10.64	7.44	48.99

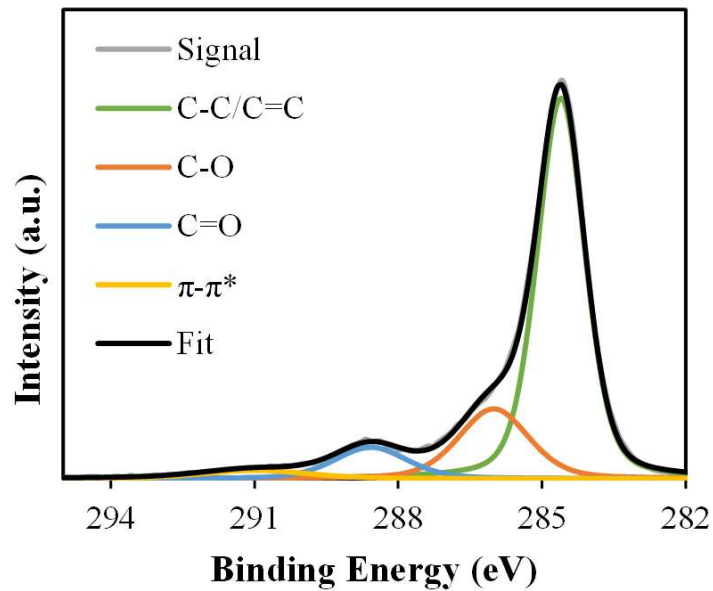


Figure 27: XPS C1s spectrum of lithium added iron-loaded graphene aerogel

In Figure 27 XPS C1s spectrum of lithium added iron-loaded graphene aerogel is given. The spectrum is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding

to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and π - π^* transition, respectively. When compared to the graphene aerogel, and iron-loaded graphene aerogels lithium addition did not affect the reduction. Carbon-oxygen single bond amount is higher in lithium added compared to iron-loaded graphene aerogels. Also, the Li1s spectrum of the lithium added samples are investigated, no signal indicating lithium presence is obtained. XPS has a low sensitivity for detecting lithium, in low concentrations, it is expected that trace amount of lithium remains undetected via XPS.

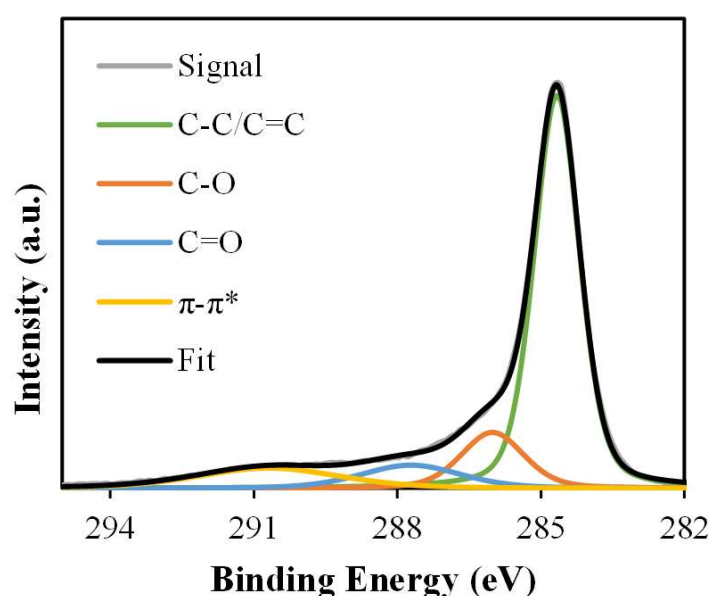


Figure 28: XPS C1s spectrum of sodium added iron-loaded graphene aerogel

In Figure 28 XPS C1s spectrum of sodium added iron-loaded graphene aerogel is given. The spectrum is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and π - π^* transition respectively. The peak at 288.0 eV is relative to lithium added samples, similar to only iron-loaded samples. π - π^* transition peak is slightly elevated

compared to iron-loaded samples. Na1s spectrum was also investigated. No signal is obtained by the Na1s spectrum.

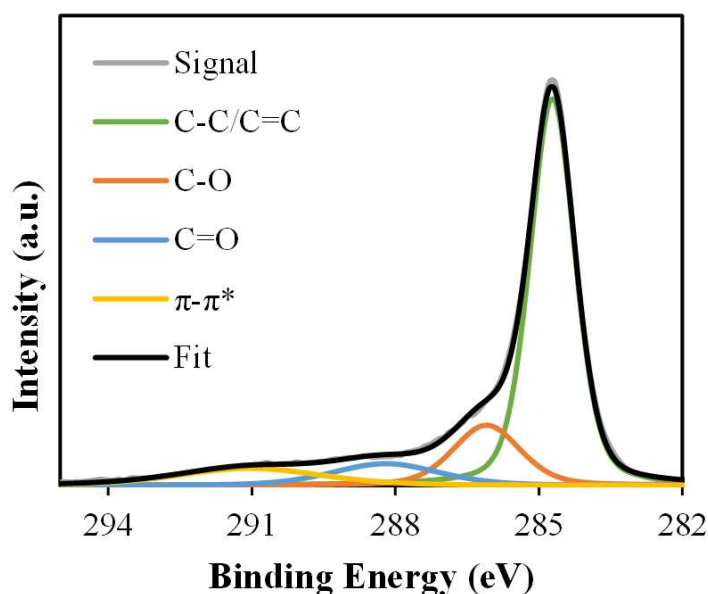


Figure 29: XPS C1s spectrum of potassium added iron-loaded graphene aerogel

In Figure 29 XPS C1s spectrum of potassium added iron-loaded graphene aerogel is given. The spectrum is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and $\pi-\pi^*$ transition respectively. The peak at 288.0 eV is relative to lithium added samples, similar to only iron-loaded samples. K2p spectrum is also investigated. No signal is obtained by the K2p spectrum.

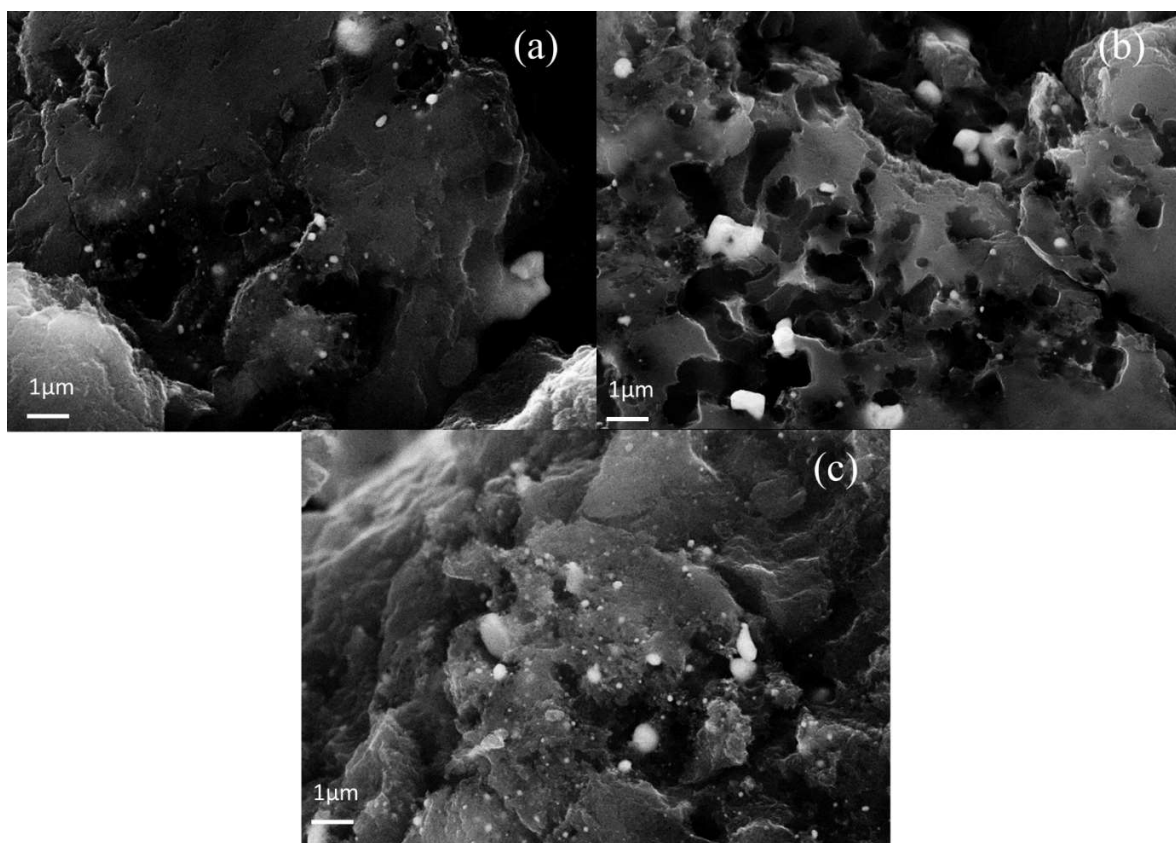


Figure 30: SEM images of lithium (a), sodium (b), and potassium (c) added iron-loaded graphene aerogels. In Figure 30 SEM images of alkali metal added iron-loaded graphene aerogels. The porous structure did not affect by the alkali metal addition. Bright spots on the images are the iron-loaded sites. Through alkali metals, lithium does not generate good contrast in SEM images⁹¹. No other metal structure is detected in the SEM.

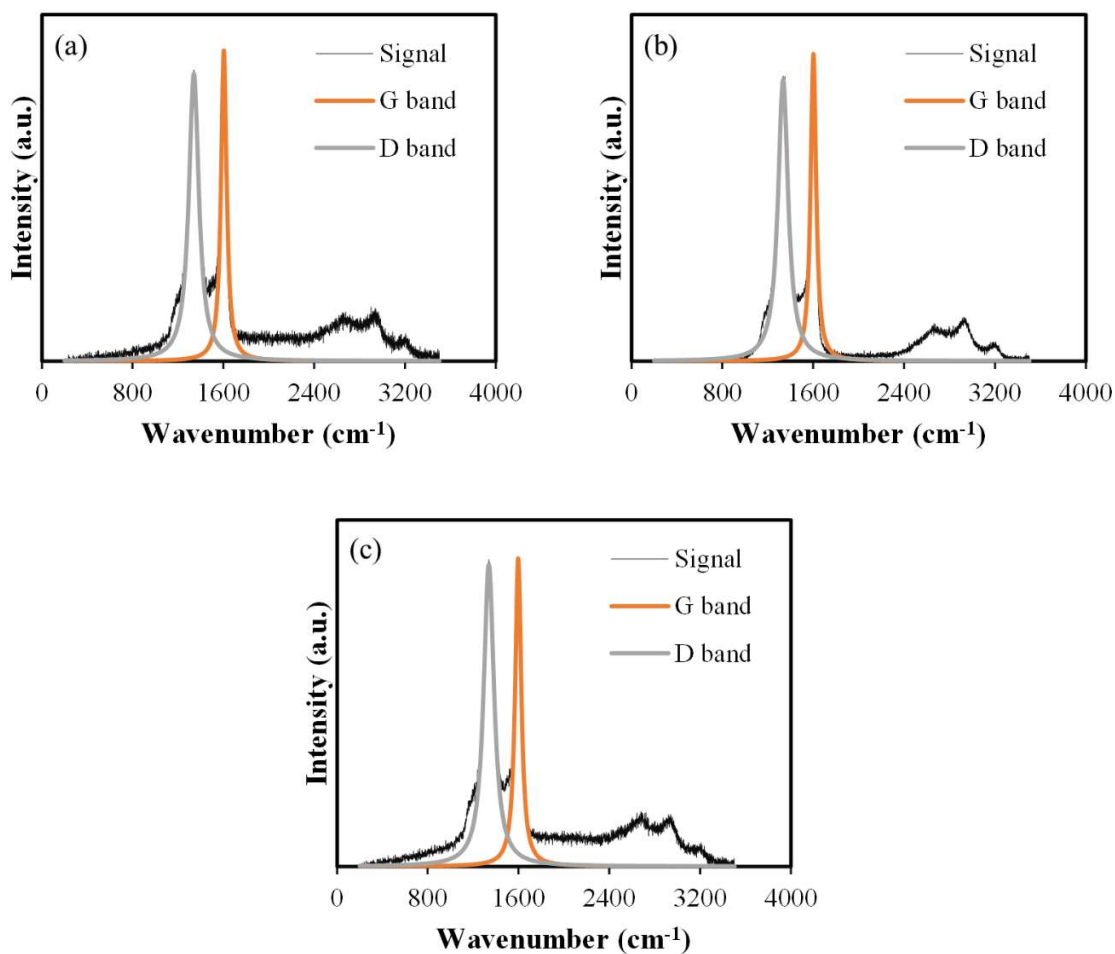


Figure 31: Raman spectrum of lithium (a), sodium (b), and potassium (c) added iron-loaded graphene aerogels. The defect ratio is deduced from Raman spectra. Raman spectra of alkali metal added iron-loaded graphene aerogels are given in Figure 31. I_D/I_G ratios are given in Table 6. The values show that alkali metal addition does not affect the reduction amount or defect amount in the graphene aerogels.

Table 6: I_D/I_G ratios of alkali metal added iron-loaded graphene aerogels

Impregnation Solution Concentration (mol/L)	Alkali Metal, and Impregnation Solution Concentration (mmol/L)	Mass Percentage of Iron (%)	I _D /I _G
0.0077	K, 2.0	8.56	1.00
0.0077	Na, 2.0	8.02	0.91
0.0077	Li, 2.0	7.44	0.92

3.3.3. Catalytic Performance of Iron Loaded Graphene Aerogels for Ammonia Decomposition Reaction

The catalytic performance of the samples is measured with the gas chromatograph as demonstrated in 3.2.7. Ammonia conversions are calculated with the equation below:

$$x\% = \frac{F_{(NH_3)_0} - F_{(NH_3)}}{F_{(NH_3)_0}} \times 100$$

F represents the flow rate of ammonia, F₀ represents the initial flow, and x represents the conversion of the ammonia. From the signals obtained by the gas chromatograph directly related to the composition of the ammonia with the help of a calibration curve, ammonia composition can be calculated. Rate of the reaction can be calculated with the following reaction:

$$r_{NH_3} = F_{(NH_3)_0} \times \frac{x}{100} \times \frac{P}{R \times T} \times \frac{1}{g_{cat}}$$

In this equation, P stands for pressure, r stands for rate, R stands for gas constant, T stands for temperature, and g_{cat} stands for the mass of the catalyst. Because of the reaction's stoichiometry rate of hydrogen production can be calculated via the following equation:

$$r_{H_2} = r_{NH_3} \times \frac{3}{2}$$

Turnover frequency is calculated via the following equation⁹².

$$D = \frac{1}{\text{Nanoparticle Size}}$$

$$TOF = \frac{r_{H_2} \times MW_{metal}}{\frac{x}{100} \times D \times 1000 \left(\frac{mmol}{mol} \right) \times 60 \left(\frac{s}{min} \right)}$$

D stands for distribution which can be calculated from the average crystal size calculated via Scherrer equation, MW stands for molar mass.

In order to calculate the activation energy of the reaction with catalyst, Arrhenius plots are drawn. These plots are generated with data below 10% ammonia conversion. The values obtained between 400-440 °C with a space velocity of 90000 mL NH₃ g_{cat}⁻¹ h⁻¹. The slope of the Arrhenius plot is $-E_a/R$ because the ammonia decomposition reaction is a zero-order reaction which makes reaction rate, and rate constant equal⁹³, activation energy is calculated with the following equation⁹⁴:

$$\ln(k) = -\frac{E_a}{RT} + \ln A$$

$$k = r$$

$$\ln(r) = -\frac{E_a}{RT} + \ln A$$

E_a represents activation energy, and A is the pre-exponential factor. In Table 7 activation energy of the reaction according to the metal loading is given. The lowest activation energy value is obtained from the 12.44% iron-loaded graphene aerogel.



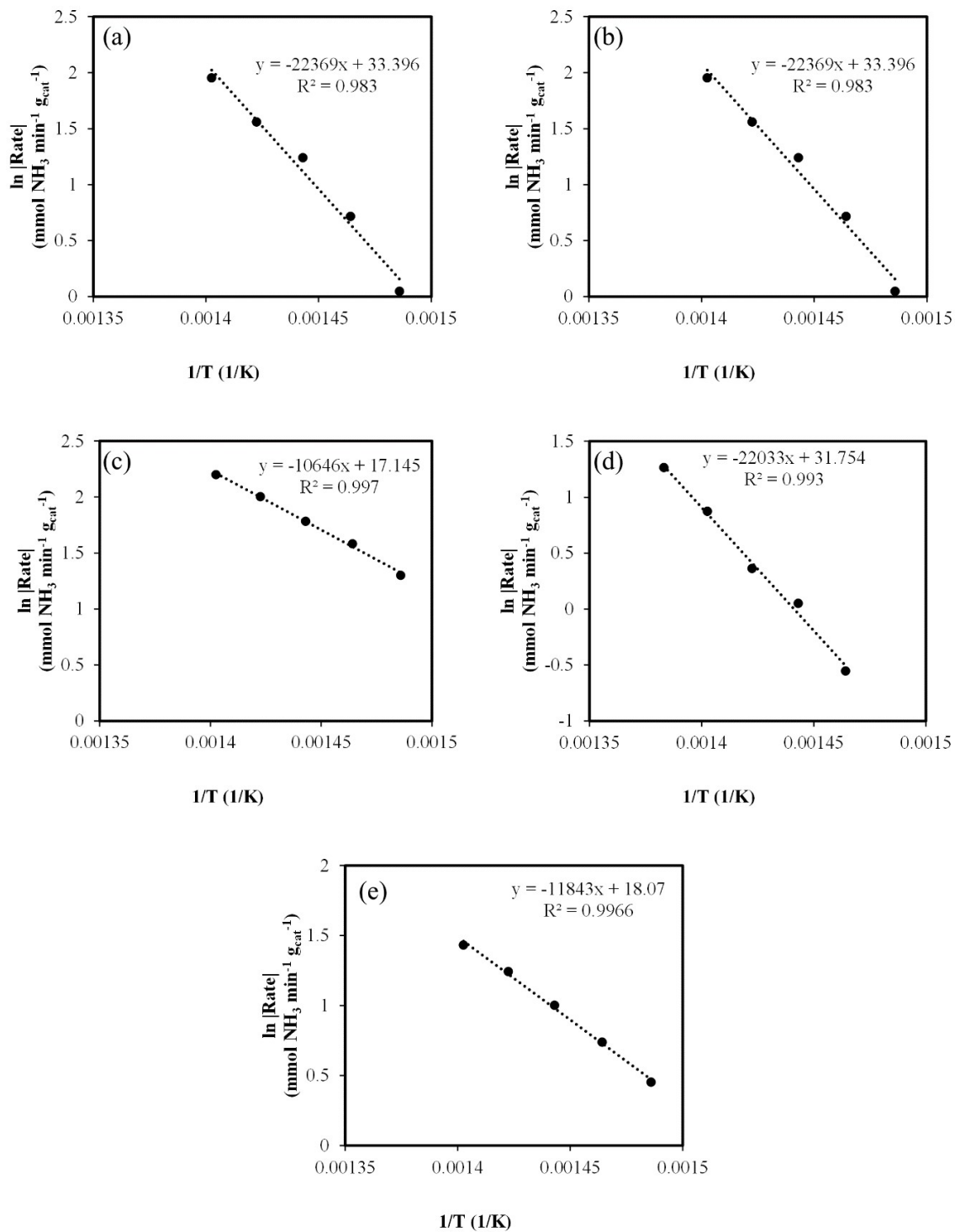


Figure 32: Arrhenius plots of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

Table 7: Different metal loading's activation energies according to Arrhenius plots

Impregnation Solution	Mass Percentage of	Activation Energy
Concentration (mol/L)	Iron (%)	(kJ/mol)
0.0077	8.12	98.46
0.015	12.26	183.17
0.03	12.44	88.51
0.06	21.33	89.01
0.1	58.34	185.97

Ammonia conversion performances of the samples are evaluated under different rates of pure ammonia flow. In Figure 33 ammonia conversion percentages of samples in a temperature gradient are given. With an increase in temperature, it is observed that the ammonia conversion amount is increased. A decrease in space velocity also increased the conversion amount. 100% ammonia conversion is achieved by 21.33% iron-loaded graphene aerogel at 600 °C, and 9000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity (Figure 33 (b)). It is observed that lower iron loading such as 8.12% iron on graphene aerogel converted 94.1% of ammonia under the same conditions (Figure 33 (e)). Conversion percentages of the samples at 600 °C are given in Figure 33. From the rate of the reaction, the production rate of H₂ is calculated. In Figure 34 results of these calculations are given. Hydrogen production rate per catalyst is reached to 101.1 mmol H₂ g_{cat}⁻¹ min⁻¹ at 600 °C with a space velocity of 180000 mL NH₃ g_{cat}⁻¹ h⁻¹ using 8.12% iron-loaded graphene aerogel. Turnover frequency is a value that in an active site reaction occurs in that frequency which can be affected by the surface area of the active sites⁹⁵. TOF value of a catalyst is affected by some variables such as the dispersion and the

size of the active particles and it represents directly the activity of the catalyst²⁰. According to the article of Yin et al., in order to compare TOF values reaction conditions must be the same⁸³. Because of the variable reaction conditions in the literature comparing the TOF values with the literature will be misleading. TOFs are calculated with the average crystal size found via the Scherrer equation and presented in Figure 35, and Table 8.



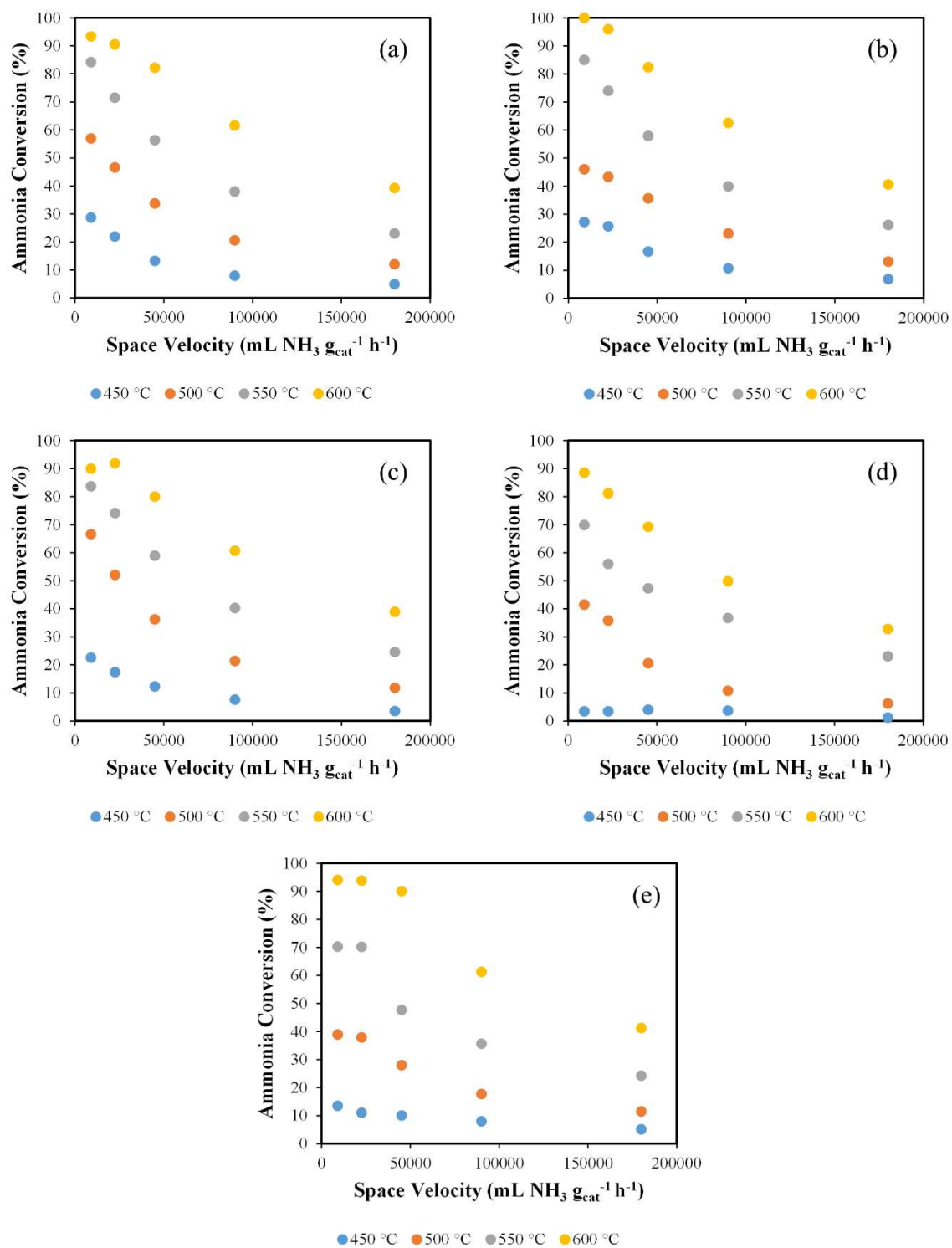


Figure 33: Ammonia conversion percentages according to different space velocity, and temperatures of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

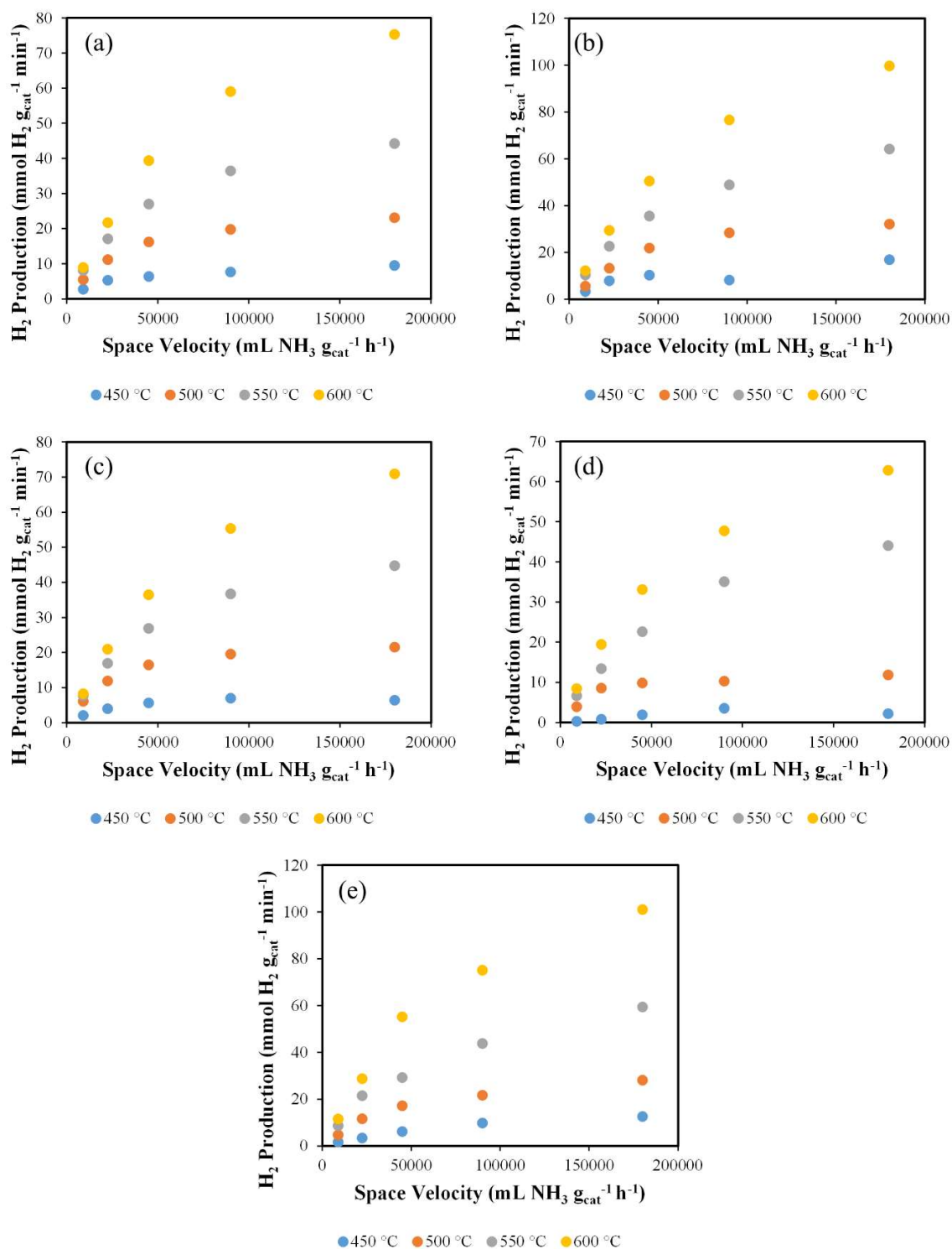


Figure 34: Hydrogen production rates according to different space velocity, and temperatures of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

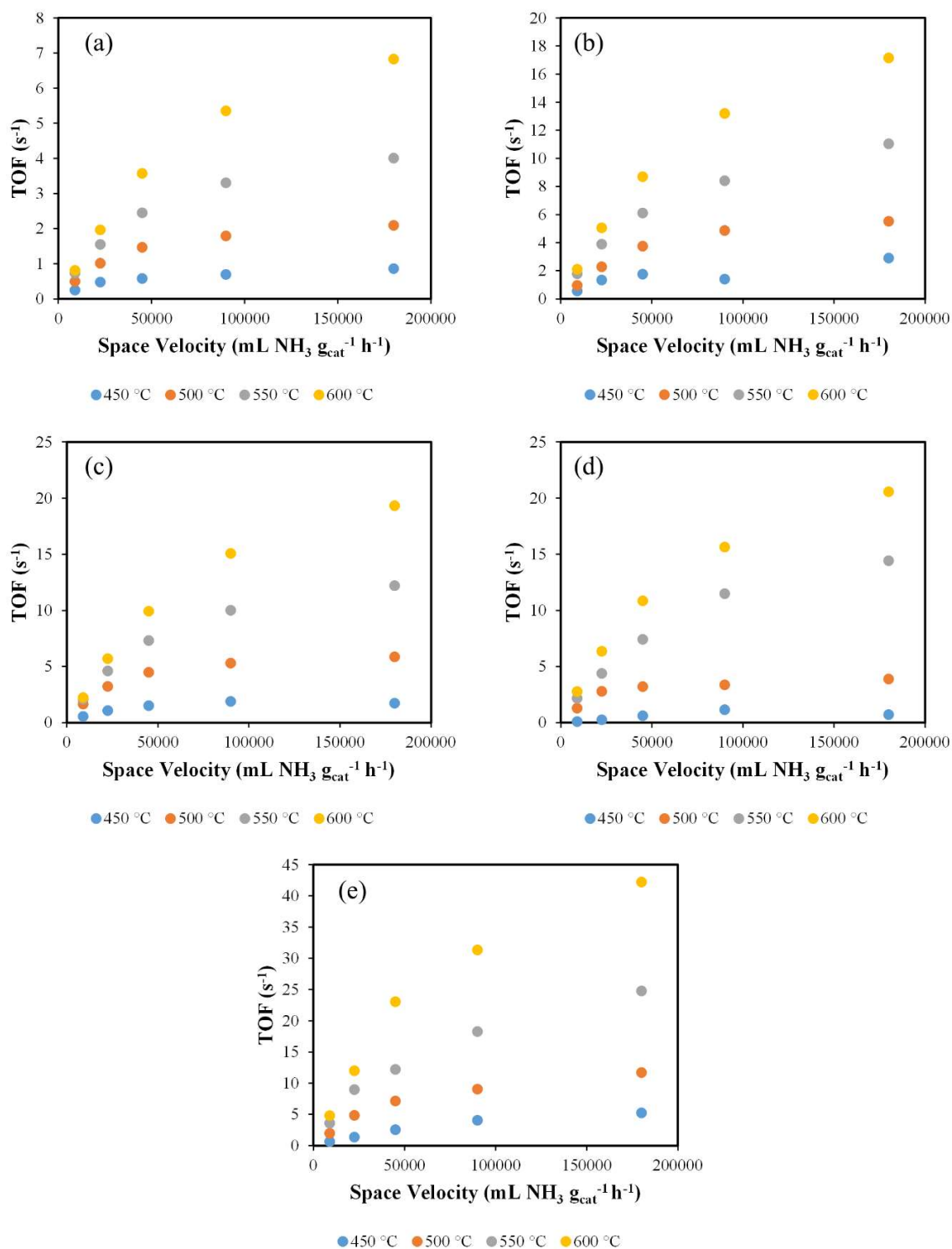


Figure 35: Turnover frequencies according to different space velocity, and temperatures of iron-loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.06 M (b), 0.03 M (c), 0.015 M (d), and 0.0077 M (e)

Table 8: Ammonia conversion percentages, hydrogen production rates, and TOF values of samples with different iron loading ratio at 600 °C

Iron Loading (%)	Space velocity (mL NH ₃ g _{cat} ⁻¹ h ⁻¹)	Ammonia conversion (%)	H2 Production Rate (mmol H ₂ g _{cat} ⁻¹ min ⁻¹)	TOF (s ⁻¹)
58.34	180000	39.3	75.3	6.8
	90000	61.63	59	5.4
	45000	82.2	39.4	3.6
	22500	90.54	21.7	2
	9000	93.4	8.9	0.8
21.33	180000	40.6	99.7	17.2
	90000	62.5	76.7	13.2
	45000	82.4	50.5	8.7
	22500	96	29.4	5.1
	9000	100	12.3	2.1
12.44	180000	38.9	86.3	23.5
	90000	60.7	64.4	17.6
	45000	80	44.2	12.1
	22500	91.9	25.5	6.9
	9000	90	11.4	3.1
12.26	180000	32.8	62.9	20.6
	90000	49.9	47.8	15.6

8.12		45000	69.2	33.1	10.8
		22500	81.19	19.4	6.4
		9000	88.5	8.5	2.8
		180000	41.2	101.1	42.2
		90000	61.2	75.1	31.4
		45000	90	55.2	23.1
		22500	93.8	28.7	12
		9000	94.1	11.5	4.8

The stability of the catalysts was evaluated at 600 °C under 45000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity for 36 hours with 21.33% iron-loaded sample. Stability measurements are made with faster flow rates, which results in lower conversion to monitor increasing or decreasing activity. In Figure 36, stability is presented. After 36 hours, the ammonia decomposition performance of the sample is changed by ±4.1%.

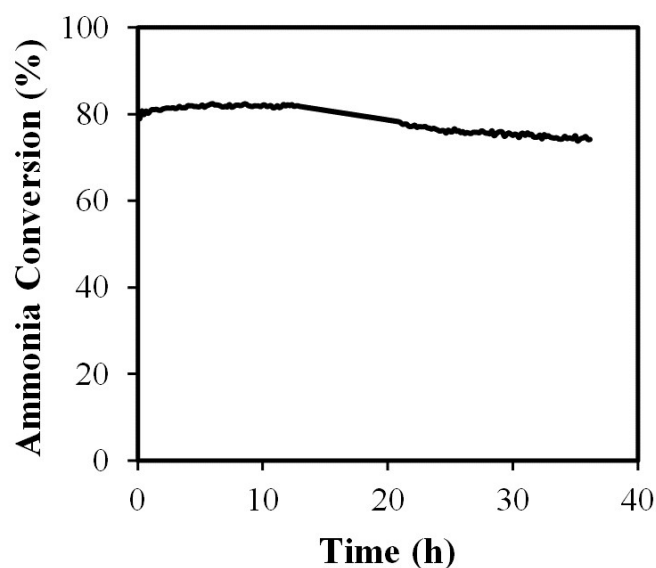


Figure 36: 21.33% iron-loaded graphene aerogel's ammonia conversion for 36 hours under 45000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity

The change in the surface chemistry of the catalyst is investigated with XPS. C1s and Fe2p_{3/2} spectra are given in Figure 37. C1s spectrum is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and π - π^* transition respectively. From that spectrum, I_{C=O}/I_{C-C}, and I_{C=O}/I_{C-C} ratios are calculated as 0.17, and 0.06 respectively. During the ammonia conversion, the C=O amount stayed similar whereas the C-O amount increased slightly. After an ammonia decomposition reaction to observe if nitrogen doping occurred, the N1s spectrum was also investigated. However, the N1s spectrum did not generate any signal. Fe2p_{3/2} spectrum presented in Figure 37 (b) is deconvoluted to 3 peaks positioned at 710.9, 714.4, and 719.0 eV binding energy. This spectrum stayed the same during the reaction when compared to the unreacted sample's spectrum. The peaks are matched with Fe₂O₃, which is confirmed with the XRD pattern of the iron-loaded catalyst after exposure to ammonia⁹⁰. In Figure 38 XRD pattern of iron catalyst after ammonia

exposure is given, peaks at $2\theta=33.2$ and 62.6° are matched with Fe_2O_3 which is parallel to the XPS result⁹⁶. Even though no nitrogen detected in XPS spectra, which is a surface analysis, Fe_2N is detected in after reaction samples of iron catalyst via XRD. The main peaks identified for Fe_2N are $2\theta = 37.6, 40.8, 42.9, 56.7, 67.8, 75.8,$ and 82.3° ⁹⁷.

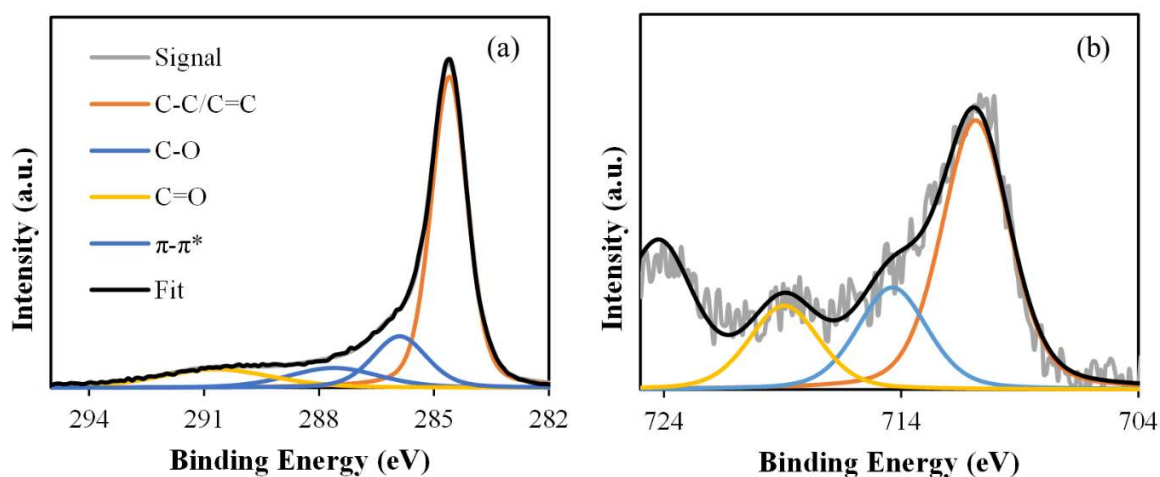


Figure 37: XPS C1s (a), and $\text{Fe}2p_{3/2}$ (b) spectra of iron-loaded graphene aerogel after ammonia decomposition reaction

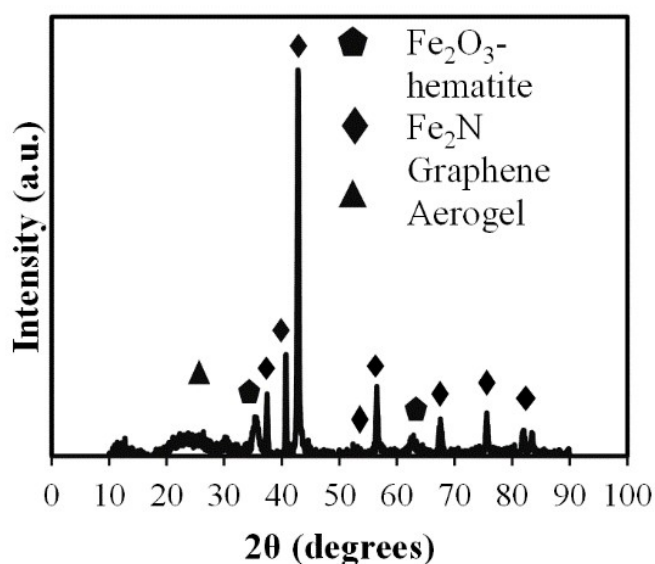


Figure 38: XRD pattern of iron-loaded graphene aerogel after ammonia decomposition reaction

For ammonia decomposition reaction iron is used in a number of works. However, none of those studies use graphene aerogel as a support material for the ammonia decomposition reaction. In this thesis by impregnation method iron-loaded onto the support material, and with concentration change loading ratio is adjusted.

In the literature, Duan et al. used carbon nanofibers as support material for 3.5% iron loading⁹⁸. At 600 °C, and 6500 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity their catalyst converted 98.9% of the ammonia. 21.33% iron-loaded graphene aerogel converted 100% ammonia at the same temperature under 9000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. When compared, the iron amount in this work is significantly higher than Duan et al.'s work. In higher space velocity 21.33% iron-loaded graphene aerogel converted ammonia at a higher rate. In another study, Li et al. used silica support instead of carbon support²². At 650 °C under 30000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity their samples reached 100% ammonia conversion. Hu et al. used silica-alumina mixtures for support material for iron-loaded catalysts⁶¹. Summary of literature is given in Table 9.

In the literature, iron catalysts are used with various support materials for ammonia decomposition reaction. The main aim of using support material is to increase the efficiency of the active iron particles. Surface area and electrical conductivity contribute the catalyst via exposing more of the active material to the reaction or enabling mobility of electrons in active sites. Another important aspect of the support material should be the thermal stability for the reactions take place in higher temperatures. In this study, graphene aerogels are used as support material because of its high surface area, electrical conductivity, and thermal stability. Results show that iron catalysts supported with graphene aerogel are showing similar ammonia conversion rates as the higher tier iron catalysts in the literature. When

metal loadings are considered, iron-loaded catalysts showed higher ammonia conversion than most of the literature. These values show that, for iron catalysts, graphene aerogels provide sufficient surface area and stability for high levels of ammonia conversion. Among other catalyst candidates, iron has a tremendous potential to compete with ruthenium. As Figure 2 demonstrates the rate constant of the ammonia decomposition with the iron catalyst is the second-highest after ruthenium with a higher energy input requirement. It is observed that graphene aerogel is enabled the potential of the iron for this reaction.

For implementing the hydrogen economy state of the art production and storage techniques of hydrogen are necessary. Efficient catalysts are one of the most important parts of this transformation. In this section of this thesis, graphene aerogel showed a promising performance as a support material for iron catalysts.

Table 9: A performance summary of iron catalyst on various support materials

Sample name	Reaction Temperature (°C)	Conversion (%)	Space velocity (mL NH ₃ g _{cat} ⁻¹ h ⁻¹)	Activation Energy (kJ/mol)	Reference
Fe@CeO ₂	650	100.0	24000	-	99
Fe@TiO ₂	650	100.0	24000	-	99
5%Fe/ZSM-5	650	98.7	30000	46	100
2.8% Fe/CNT	700	75.1	5000	-	101
Fe ₂ N/CNTs	500	85.3	6000	-	102
Fe ₂ N/SBA-15	500	56.3	6000	-	102
Fe/CNT	500	0.47	30000	148.5	25
2%Fe-Coal Char	750	100.0	45000	-	103
Fe-CNFs/mica	600	98.9	6500	93.5	98
Fe ₁₀ /Y doped ZrO ₂	700	70.0	46000	-	104
Nano Fe@micro-SiO ₂	670	100.0	30000	-	22
Nano Fe@meso- SiO ₂	650	100.0	30000	-	22
Carbon Silica-Fe	670	100.0	7500	-	56
Red Mud	700	98.8	120000	136.5	105

3.3.4. Catalytic Performance of Alkali Metal Added Iron Loaded Graphene Aerogels for Ammonia Decomposition Reaction

Catalytic performance measurements of the alkali metal loaded samples are measured with the gas chromatograph, same as the iron-loaded graphene aerogels. Conversion, rate, H₂ production rate, TOF, and activation energy calculations are made with equations presented in 3.3.3. Arrhenius plots are given in Figure 39. From slopes of the plots activation energy of the reaction can be calculated. Activation energies are presented in Table 10.

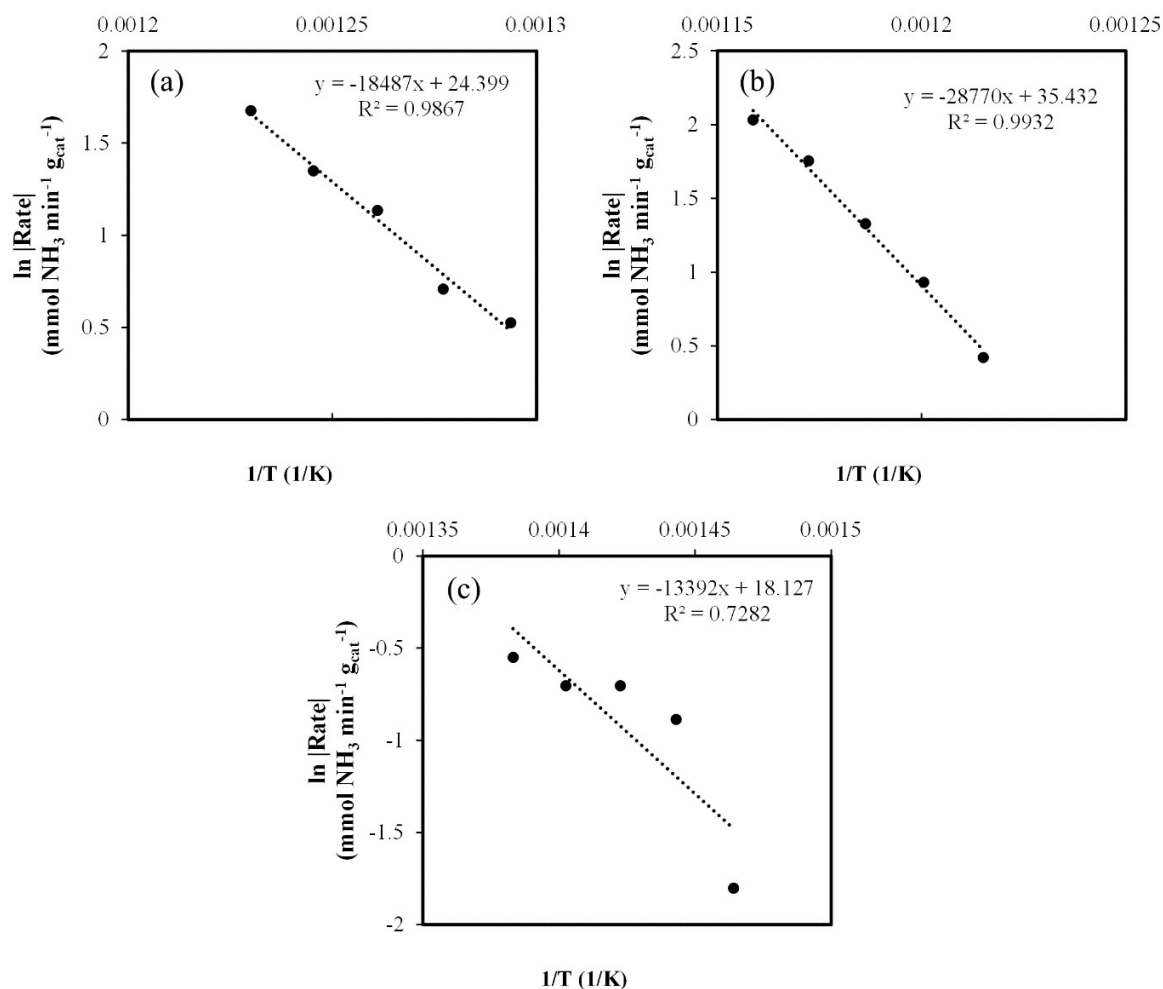


Figure 39: Arrhenius plots of lithium, sodium, and potassium added iron-loaded graphene aerogels

Table 10: Different alkali metal additive's activation energies according to Arrhenius plots

Impregnation Solution Concentration (mol/L)	Alkali Metal, and Impregnation Solution Concentration (mmol/L)	Mass Percentage of Iron (%)	Activation Energy (kJ/mol)
0.0077	K, 2.0	8.56	111.3
0.0077	Na, 2.0	8.02	239.2
0.0077	Li, 2.0	7.44	153.7

Ammonia conversion performances are measured temperatures up to 600 °C, and flow between 9000, and 180000 mL NH₃ g_{cat}⁻¹ h⁻¹, and presented in Figure 40. Alkali metal added iron-loaded graphene aerogels are performed significantly less than plain iron-containing catalysts. Lithium added catalyst converted 79.3%, sodium added catalyst converted 43.2%, and potassium added catalyst converted 73.3% of the ammonia at 600 °C under 9000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. Only iron-containing catalyst with the same loading converted 94.1% of the ammonia in the same conditions. The highest conversion is achieved by the potassium added catalyst. Hydrogen production rates are presented in Figure 41. The highest hydrogen production rate is achieved by lithium added catalyst at 600 °C under 180000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. TOF values are presented in Figure 42. Highest TOF is recorded by lithium added catalyst by 18.3 s⁻¹. Conversion percentages, hydrogen production rates, and TOFs of the samples at 600 °C are given in Table 11.

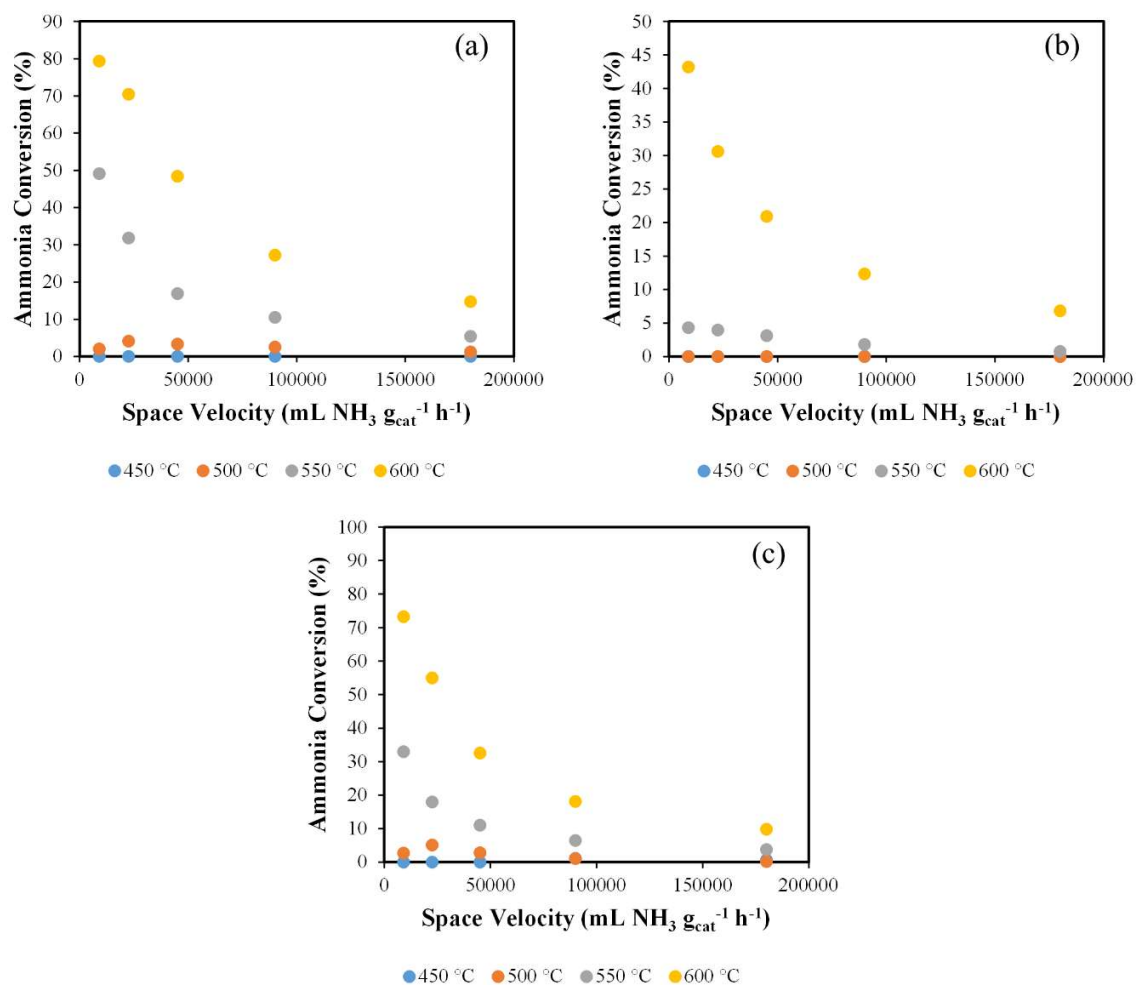


Figure 40: Ammonia conversion amounts according to different space velocity, and temperatures of alkali metal added iron-loaded graphene aerogels, Li (a), Na (b), and K (c)

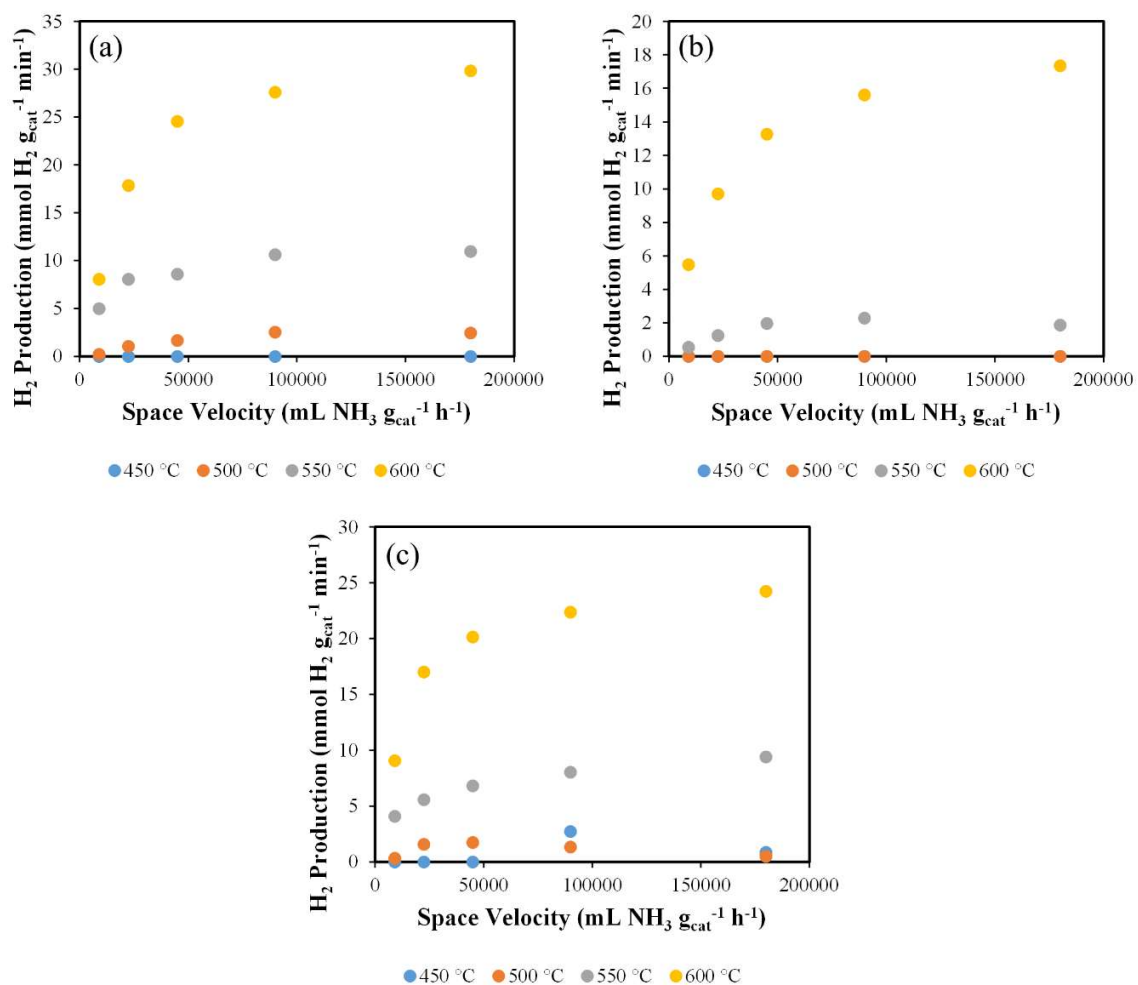


Figure 41: Hydrogen production rates according to different space velocity, and temperatures of alkali metal added iron-loaded graphene aerogels, Li (a), Na (b), and K (c)

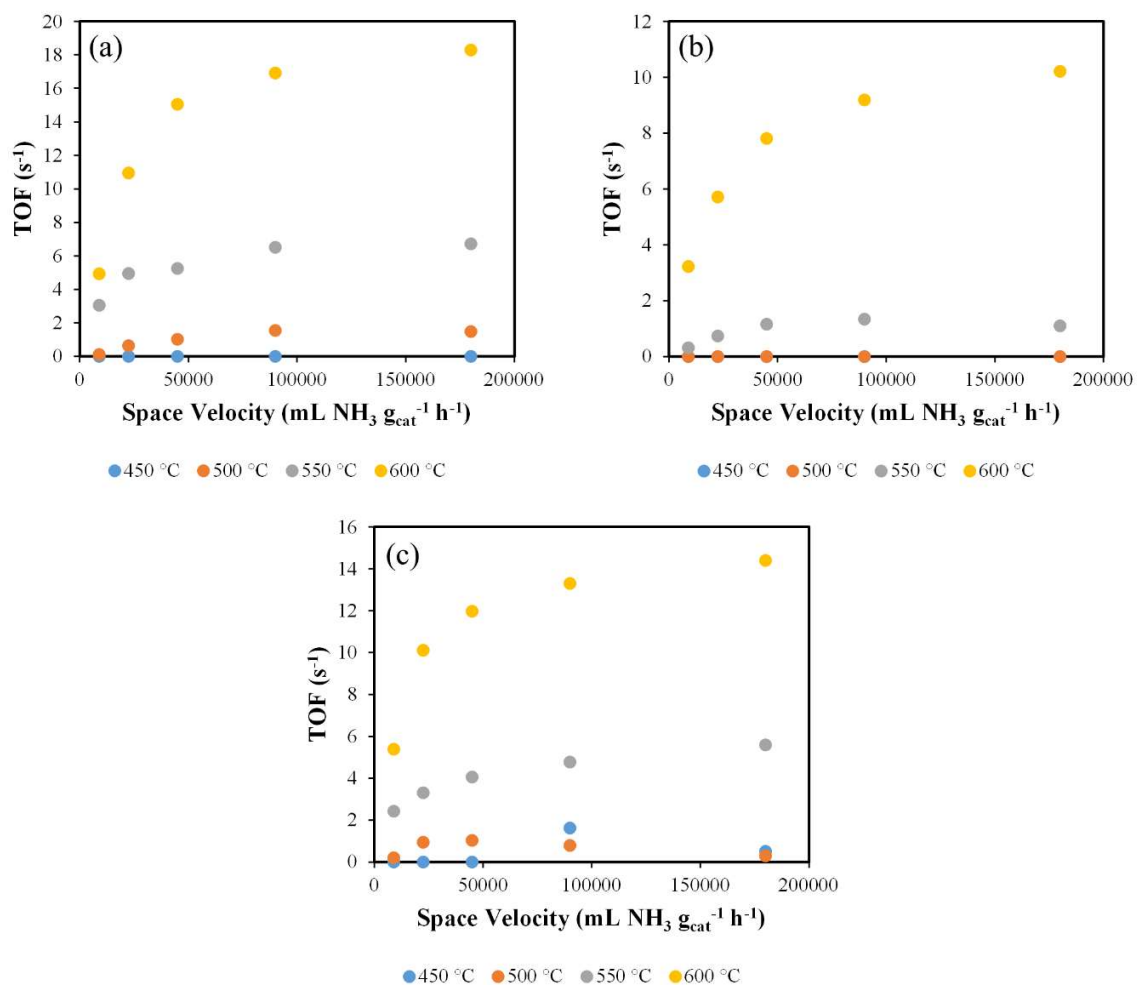


Figure 42: Turnover frequencies according to different space velocity, and temperatures of alkali metal added iron-loaded graphene aerogels, Li (a), Na (b), and K (c)

Table 11: Ammonia conversion percentages, hydrogen production rates, and TOF values of samples with different alkali metal addition at 600 °C

Sample	Space velocity (mL NH ₃ g _{cat} ⁻¹ h ⁻¹)	Ammonia conversion (%)	H2 Production Rate (mmol H ₂ g _{cat} ⁻¹ min ⁻¹)	TOF (s ⁻¹)
Fe- Li/GA	180000	14.7	29.8	18.3
	90000	27.2	27.6	16.9
	45000	48.4	24.6	15.1
	22500	70.4	17.9	10.9
	9000	79.3	8	4.9
Fe- Na/GA	180000	6.83	17.3	10.2
	90000	12.3	15.6	9.2
	45000	20.9	13.3	7.8
	22500	30.6	9.7	5.7
	9000	43.2	5.5	3.2
Fe- K/GA	180000	9.8	24.2	14.4
	90000	18.1	22.4	13.3
	45000	32.6	20.1	12
	22500	55	17	10.1
	9000	73.25	9.1	5.4

In the literature, iron is used as a catalyst for ammonia decomposition reaction. However, no study is used alkali metals to improve the performance of the catalyst. Because of that results

are not comparable. On the other hand, compared with the catalyst contains iron only, the significant performance loss is observed. The addition of an alkali metal promoter has several effects on the catalyst surface such as increasing the surface area, increasing the electron mobility near active sites, or preventing the sinteration of active metals^{19,106}. There are various instances that these promoters negatively affect catalytic activity. Due to the lack of investigation in the literature on alkali metal promoted iron catalysts the reason for this decline in the catalytic activity remain unexplained.

3.4. Conclusion

In this chapter synthesized graphene aerogels are decorated with iron via the impregnation method. The concentration of the impregnation solution controlled the iron loading ratio. The thermal reduction is performed to the catalyst in order to break carbon-oxygen bonds. Catalysts' metal loadings are determined via TGA and XRD. Surface chemistry, oxidation state, and defect sites are investigated with XPS, XRD, and Raman. Morphology is investigated with SEM. Alkali metal addition is investigated via XPS, and XRD no signals corresponding alkali metals are found. Iron loaded catalysts performed comparably to a higher tier of catalysts that performed high ammonia conversion in similar conditions. 21.33% iron-loaded catalyst converted 100% of the ammonia at 600 °C under 9000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. Even though the alkali metal presence detected by characterization, its effect on ammonia conversion is clear.

Chapter 4: Cobalt Loaded Graphene Aerogels as a Catalyst for Ammonia Decomposition Reaction

4.1. Introduction

The surface area of graphene oxide makes it an interesting catalyst support material. Another aspect of graphene is metal nanoparticle decoration on it can be carried out with a number of options²⁶. Electroless plating of metals on graphene¹⁰⁷, vapor transport¹⁰⁸, anchoring on polymer matrix¹⁰⁹, and impregnation¹¹⁰ are some of the popular metal loading methods on graphene. In this chapter, the impregnation method is used to decorate graphene aerogels with cobalt particles. Differences in the impregnation solution help the metal loading ratio on the material as seen in 3.3.1. Cobalt is used for ammonia decomposition reaction however, catalytic performance is not enough to replace expensive catalysts^{21,60}. Aim of the production of cobalt loaded catalysts is reducing the high temperature or expensive catalyst requirements of ammonia decomposition reaction. In some studies, cobalt catalysts showed similar catalytic activity for ammonia decomposition reaction^{21,60} with other transition metal catalysts^{20,111}. However, the amount of studies is very limited compared to nickel, iron, and ruthenium. Because of the potential of cobalt catalysts, and the high surface area, stability, and electrical conductivity of graphene aerogel catalytic performance for ammonia decomposition reaction of cobalt loaded graphene aerogel are measured. Also, the aforementioned improvement possibility of catalytic activity via alkali metal addition on different studies may help improve cobalt catalysts' catalytic performance. In this chapter, cobalt nanoparticles are loaded on graphene aerogels. The thermal reduction is applied. Catalytic ammonia decomposition performances are measured with and without alkali metal addition.

4.2. Materials, and Procedure

4.2.1. Materials

99.9995% graphite produced by Alfa Aesar is used as a precursor. For the oxidation of graphite, NaNO_3 from Alfa Aesar, KMnO_4 , and H_2O_2 (30%) from Merck Millipore, HCl (37%), and H_2SO_4 (95-97%) from Sigma Aldrich are obtained. For solvent exchange 99% ethanol from Isolab. For the cobalt loading, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.0%) from Merck Millipore are used. NaCl and KCl purchased from Merck Millipore, LiCl purchased from Sigma Aldrich. In all the procedures distilled water with 18.2 M Ω electrical resistance is used.

4.2.2. Graphene Oxide

Graphene oxide solution is used in this chapter to synthesize aerogels. Details of graphene oxide synthesis are given in Section 2.2.2.

4.2.3. Graphene Aerogel

Graphene alcogels are used in this chapter to load metals by impregnation. Details of graphene aerogel synthesis are given in Section 2.2.3.

4.2.4. Cobalt Loading on Graphene Aerogels

Metals are loaded via the impregnation method in the impregnation solution. Impregnation solutions are prepared with ethanol and precursor cobalt salt. After the solvent exchange, alcogels are dipped in the precursor solutions. The precursor salt used in this work is $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. A gradient of impregnation solutions is used to control the metal loading ratio. This gradient consists of concentrations of 0.1, 0.075, 0.05, 0.0125, and 0.0025 M. Alkogels stayed 24h in precursor solutions to complete the metal loading. After metal

loading, alcogels are dried via the aforementioned supercritical CO₂ drying under the same conditions with iron loaded catalysts. The thermal reduction is applied to the cobalt loaded aerogels to reduce partially reduced carbon support and cobalt particles. Thermal reduction conditions for cobalt loaded graphene aerogels are the same as iron-loaded catalysts, with the exception of temperature. The reduction temperature of cobalt loaded catalysts is 600 °C. Drying and thermal reduction are described in 3.2.4.

4.2.5. Alkali Metal Addition on Cobalt Loaded Graphene Aerogels

Alkali metal addition is made via alkali metal salt addition to 0.1 M Co(NO₃)₂·6H₂O impregnation solution. Alkali metal salt concentrations are 5.3mM in the impregnation solution. Alkali metal salts used are LiCl, NaCl, and KCl. Drying, and thermal reduction conditions are as described in 4.2.4.

4.2.6. Characterization of Cobalt Loaded Aerogels

Cobalt loadings are determined via TGA under dry air. With oxygen, and high heat graphene aerogels completely turned into gas. The only remaining solid is oxidized cobalt. Remaining cobalt oxide is determined via XRD. By the mass of remaining metal oxide, the mass percentage of loaded cobalt ratio can be calculated. XRD is used to determine the loaded metals' state. Surface chemistry is investigated with XPS. Raman is used for the investigation of defects. Morphology is investigated under SEM. The same procedures are applied to alkali metal added catalysts to investigate the changes between only cobalt loaded catalysts.

4.2.7. Catalytic Performance Measurements of Cobalt Loaded Graphene Aerogels

Catalytic performance measurements are made via GC and MFC. Cobalt loaded graphene aerogels are placed in a quartz tube stabilized with quartz wool as the diagram in Figure 16. The thermal reduction is carried out in the reaction system before data collection. Data

collection is done under pure NH_3 flow. Catalytic performance measurements are made via gas chromatograph and mass flow controller. Iron loaded graphene aerogels are placed in a quartz tube stabilized with quartz wool as the diagram in Figure 16 shows. In situ thermal reduction is carried out in the reaction system before data collection. Data collection is done under pure NH_3 flow. A gradient of reaction temperatures and a gradient of space velocity of NH_3 is used in data collection. The temperature gradient used is 450, 500, 550, and 600 °C, whereas the space velocity gradient is between 10000, and 1200000 $\text{mL NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$. For every reaction temperature, ammonia conversion data are collected for every space velocity in the gradient. Conversion data are calculated from NH_3 area measured by GC or flow rate measured by MFC according to the suitable calibration curve. A detailed calibration procedure is given in 3.2.7.

4.3. Results, and Discussion

4.3.1. Properties of Cobalt Loaded Graphene Aerogels

Cobalt loading ratios of cobalt loaded graphene aerogels are determined via TGA. TGA is performed under dry air flow, and the temperature is increased to 800 °C. The carbon part of the catalyst turned into gaseous CO and CO_2 . The remaining solid is cobalt oxide. To calculate the initial cobalt amount in the catalysts, the phase of cobalt oxide needs to be determined. TGA graphs are presented in Figure 43. XRD pattern of the residual cobalt oxide is presented in Figure 44. Peaks at $2\theta = 19.0, 31.3, 36.9, 38.5, 44.8, 59.4,$ and 65.2 degrees are matched with Co_3O_4 (JCPDS No: 42-1467)¹¹². The initial cobalt amount can be deducted from the final metal oxide mass. In Figure 45 XRD patterns of catalysts are given. The peaks are matched with graphene aerogel, metallic cobalt, and cobalt oxide. The peak at $2\theta = 26^\circ$ graphene aerogel peak is present, the location of the peak is consistent with the

characterization of the graphene aerogel in 2.3.2. Peaks at $2\theta = 44.2, 51.5,$ and 75.9 degrees are matched with metallic cobalt (JCPDS No: 15-0806)¹¹³. Because of the time catalysts expose to the air oxidation of the metals on the surface is possible. Additional to graphene aerogel, and metallic cobalt, CoO peaks are observed in XRD patterns. Peaks at $2\theta = 36.5$ and 42.4 degrees are matched with CoO (JCPDS No: 48-1719)¹¹⁴. Average crystal sizes are calculated via the Scherrer equation. The sharpest peak of metallic cobalt is at $2\theta = 44.2^\circ$, a peak of CoO is interfering with the peak. Fitting is made before using the Scherrer equation to eliminate the error. Average crystal sizes and cobalt loadings of the catalysts are given in Table 12.

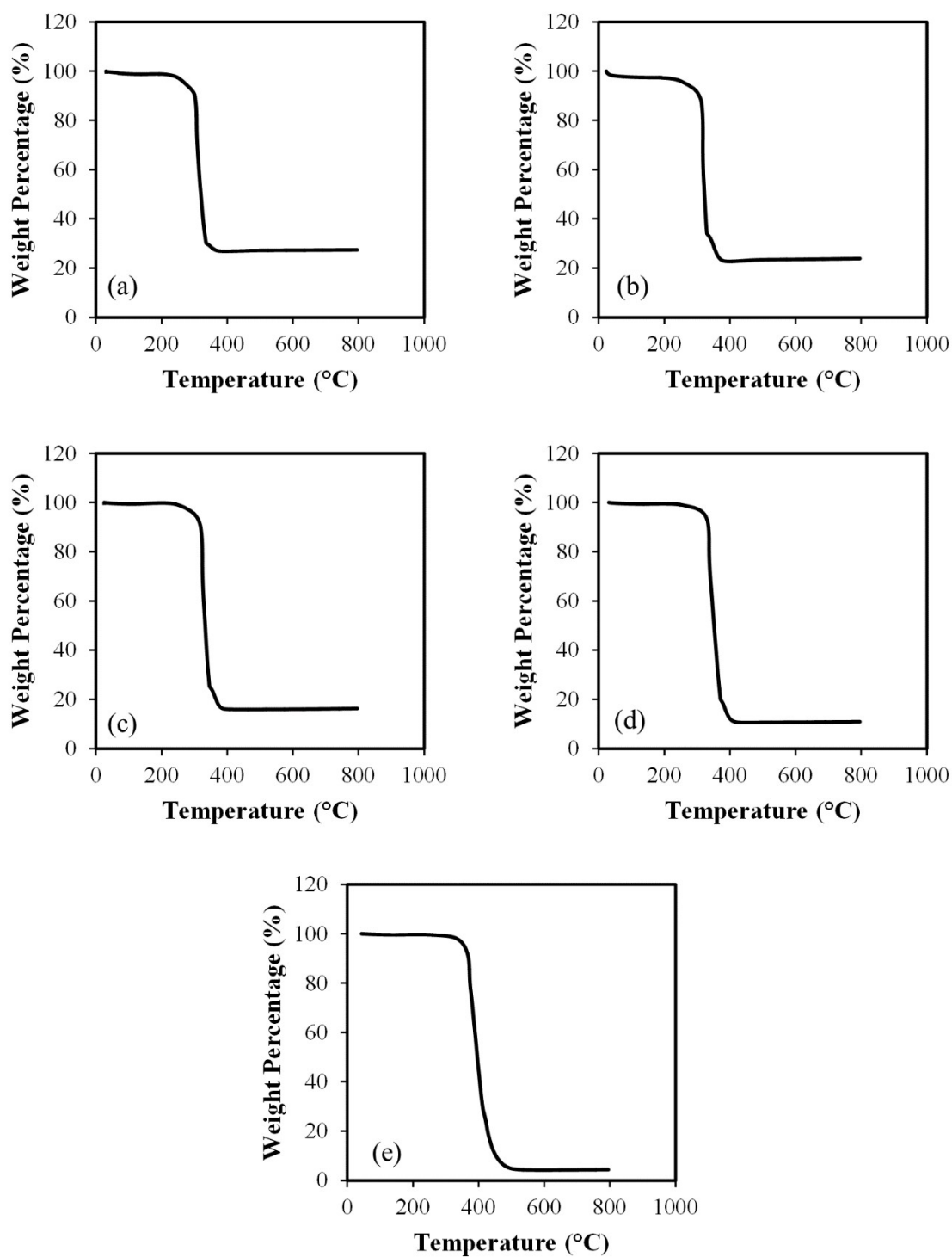


Figure 43: TGA graphs of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

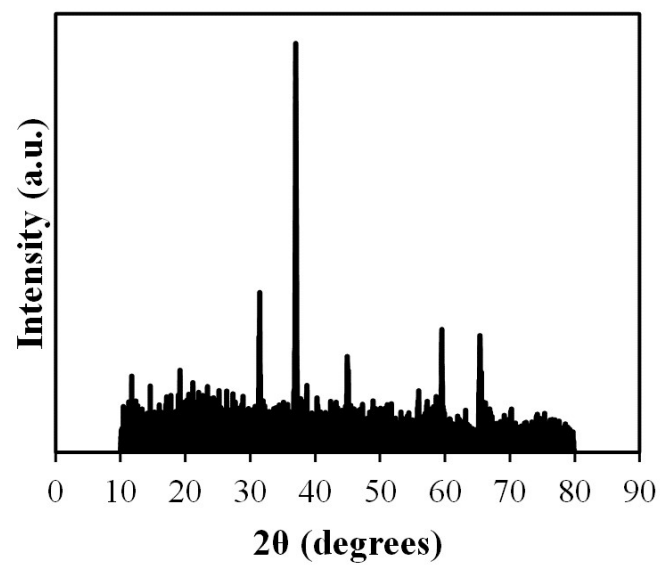


Figure 44: XRD pattern of the residual metal oxide from TGA

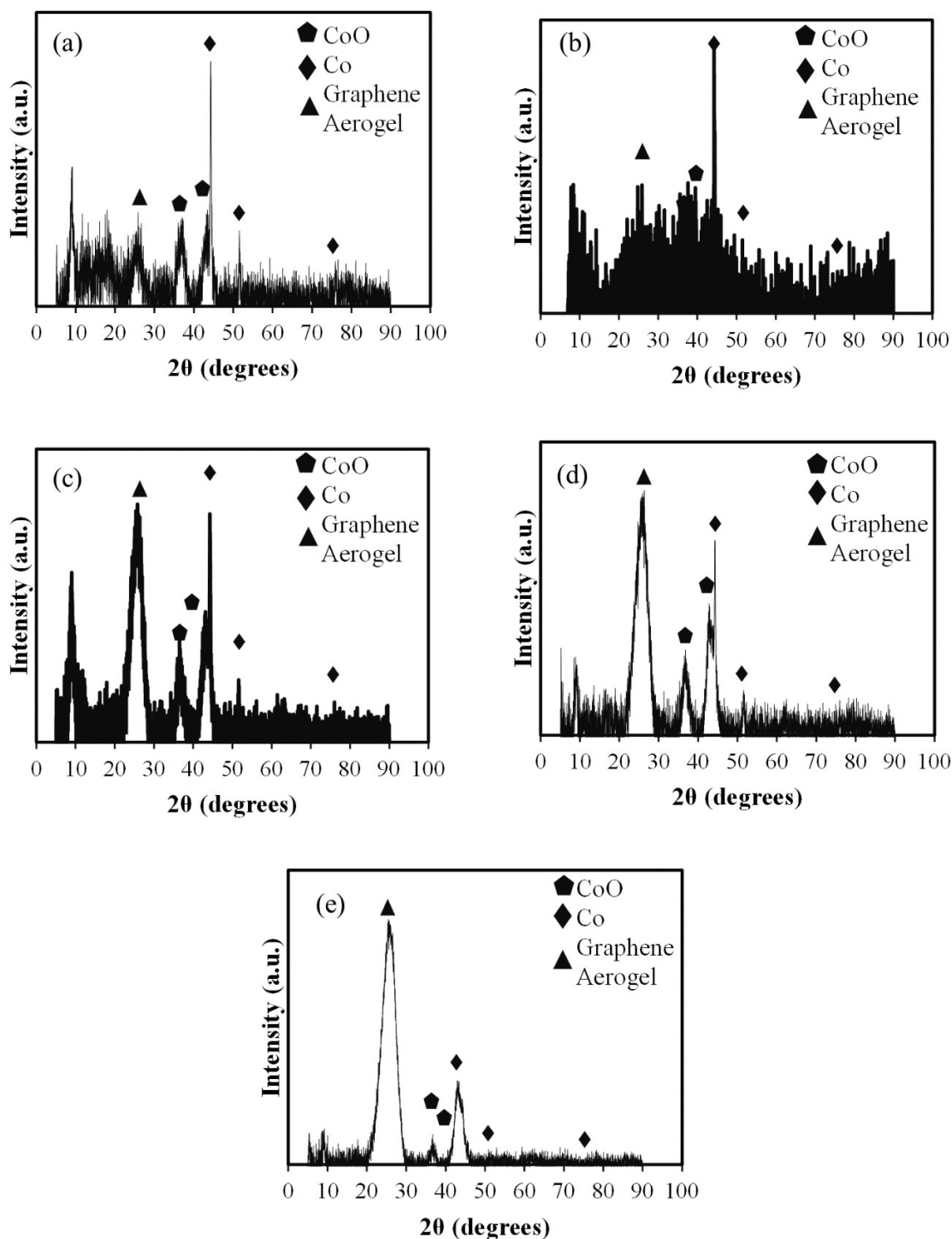


Figure 45: XRD patterns of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

Table 12: Cobalt loading ratios according to the samples' impregnation solution concentration, and average crystal size of cobalt according to Scherrer Equation

Impregnation Solution Concentration (mol/L)	Mass Percentage of Cobalt Oxide (Co₃O₄) (%)	Mass Percentage of Cobalt (%)	Average Cobalt Crystal Size (nm)
0.0025	4.35	3.19	92.35
0.0125	10.88	7.98	22.52
0.05	16.29	11.78	21.5
0.075	23.89	17.28	135.8
0.1	27.40	20.11	27.82

The surface chemistry of the catalysts is investigated with XPS. C1s and Co2p_{3/2} spectra are investigated. In Figure 46 (a) XPS C1s spectrum of the catalyst is given. This spectrum is deconvoluted to four peaks at 84.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and π - π^* transition respectively, same as graphene aerogel, and iron-loaded catalysts. $I_{C=O}/I_{C-C}$ ve $I_{C=O}/I_{C-C}$ ratios are calculated as 0.14, and 0.05 respectively. These values show that reduction did not affect by the cobalt loading since the values are similar to thermally reduced graphene aerogel. The cobalt spectrum is given in Figure 46 (b) deconvoluted to three peaks located at 780.0, 782.6, and 787.2 eV. These peaks are representing the +2 oxidation state of cobalt which is bound to oxygen³³. The oxidation may occur because of the same reason with iron-containing catalysts, high energy x-rays.

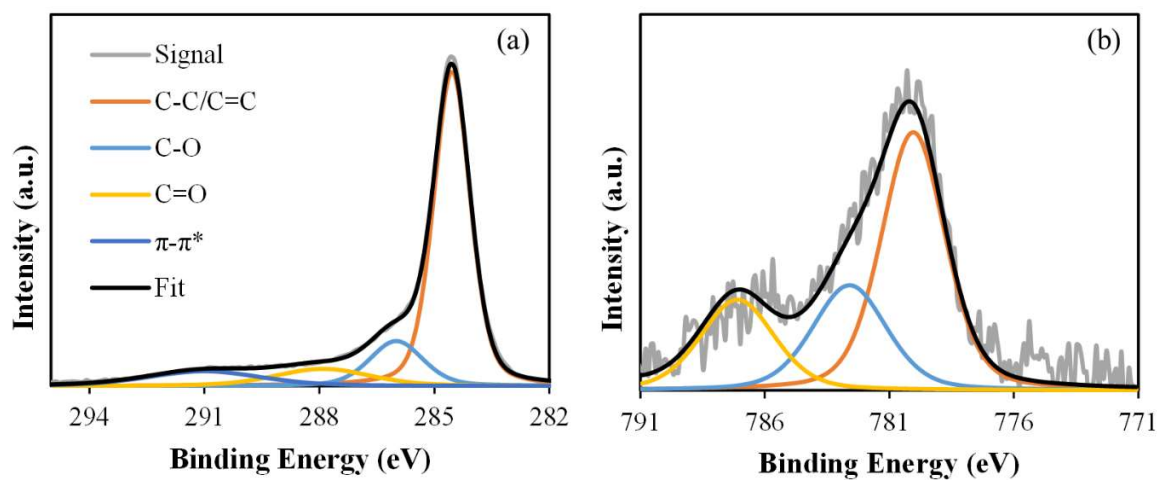


Figure 46: XPS C1s (a), and Co2p_{3/2} (b) spectra of thermally reduced cobalt loaded graphene aerogel

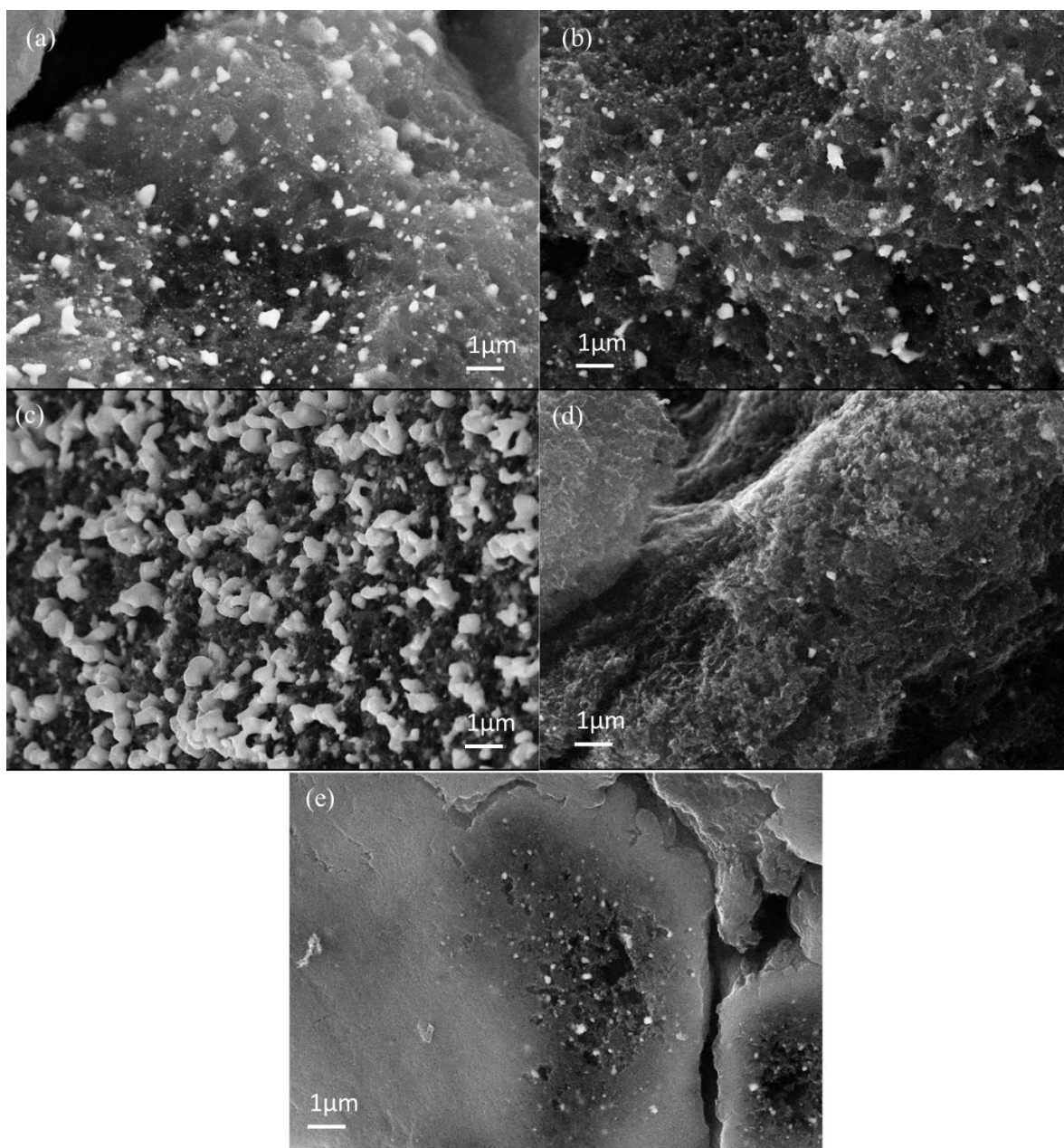


Figure 47: SEM images of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

In Figure 47 SEM images of the cobalt loaded catalysts are given. SEM images show that the porous structure of the graphene aerogel stayed after thermal reduction and the cobalt loading of the catalysts. Defect ratios are investigated with Raman. Raman spectra are given in Figure 48. The spectra are deconvoluted to two peaks corresponding D, and G bands. The

ratio of I_D/I_G gives the defect ratio. I_D/I_G ratios are presented in Table 13. D band represents the defects of the support material. According to the ratios, metal loading did not affect the defect amounts.



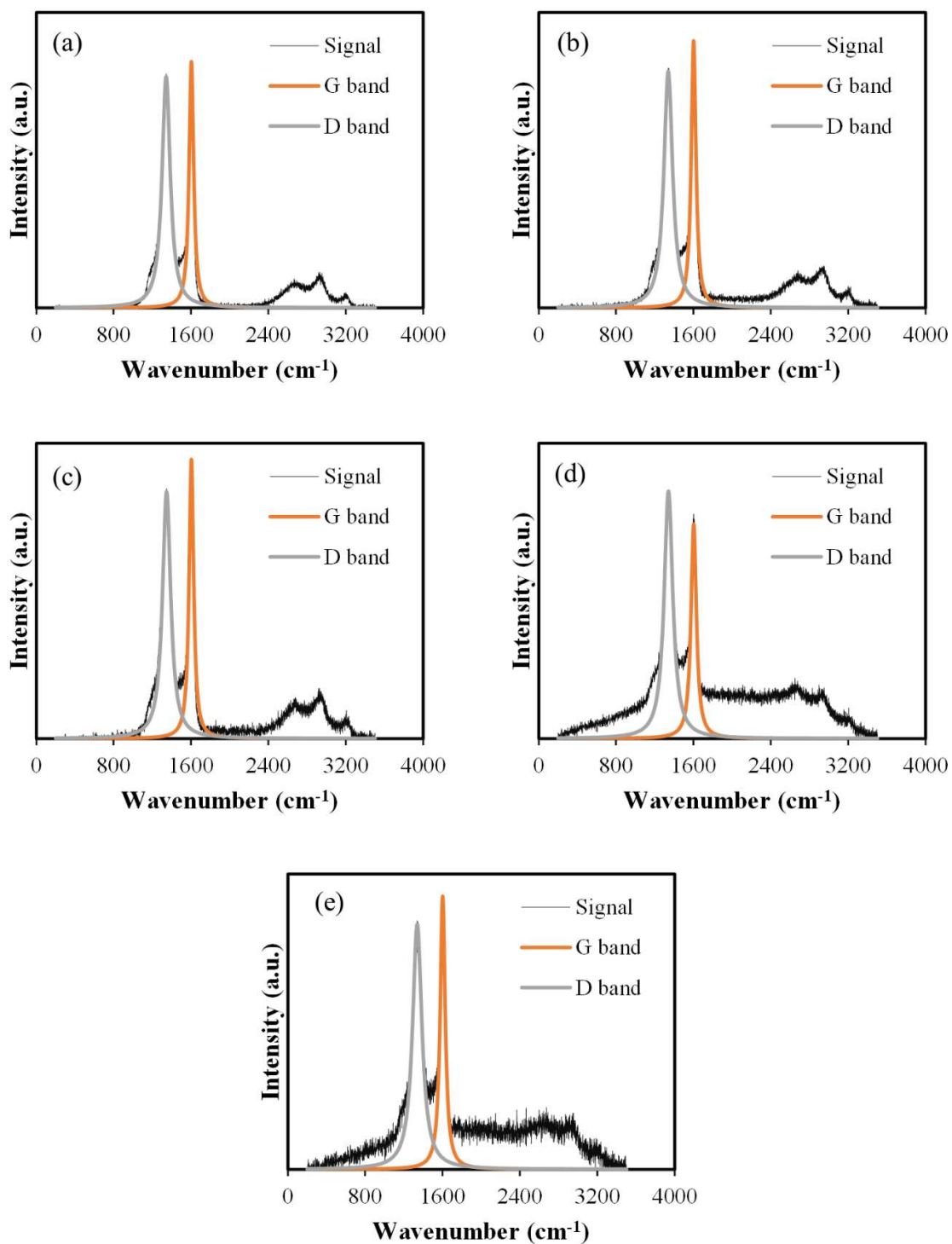


Figure 48: Raman spectra of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

Table 13: I_D/I_G ratios of cobalt loaded graphene aerogels

Impregnation Solution Concentration (mol/L)	Mass Percentage of Cobalt (%)	I_D/I_G
0.0025	3.19	0.91
0.0125	7.98	1.10
0.05	11.78	0.89
0.075	17.28	0.89
0.01	20.11	0.95

4.3.2. Properties of Alkali Metal Added Cobalt Loaded Graphene Aerogels

Alkali metal added cobalt loaded catalysts' metal loadings are determined via TGA. The same technique with 4.3.1 applied. TGA graphs are presented in Figure 49. XRD patterns presented in Figure 50 shows no trace of alkali metals. Similar to only cobalt loaded catalysts, Co, CoO, and graphene aerogel peaks are detected. Crystal sizes are calculated via the Scherrer equation using the sharpest metallic cobalt peak. TGA results and crystal sizes are presented in Table 14

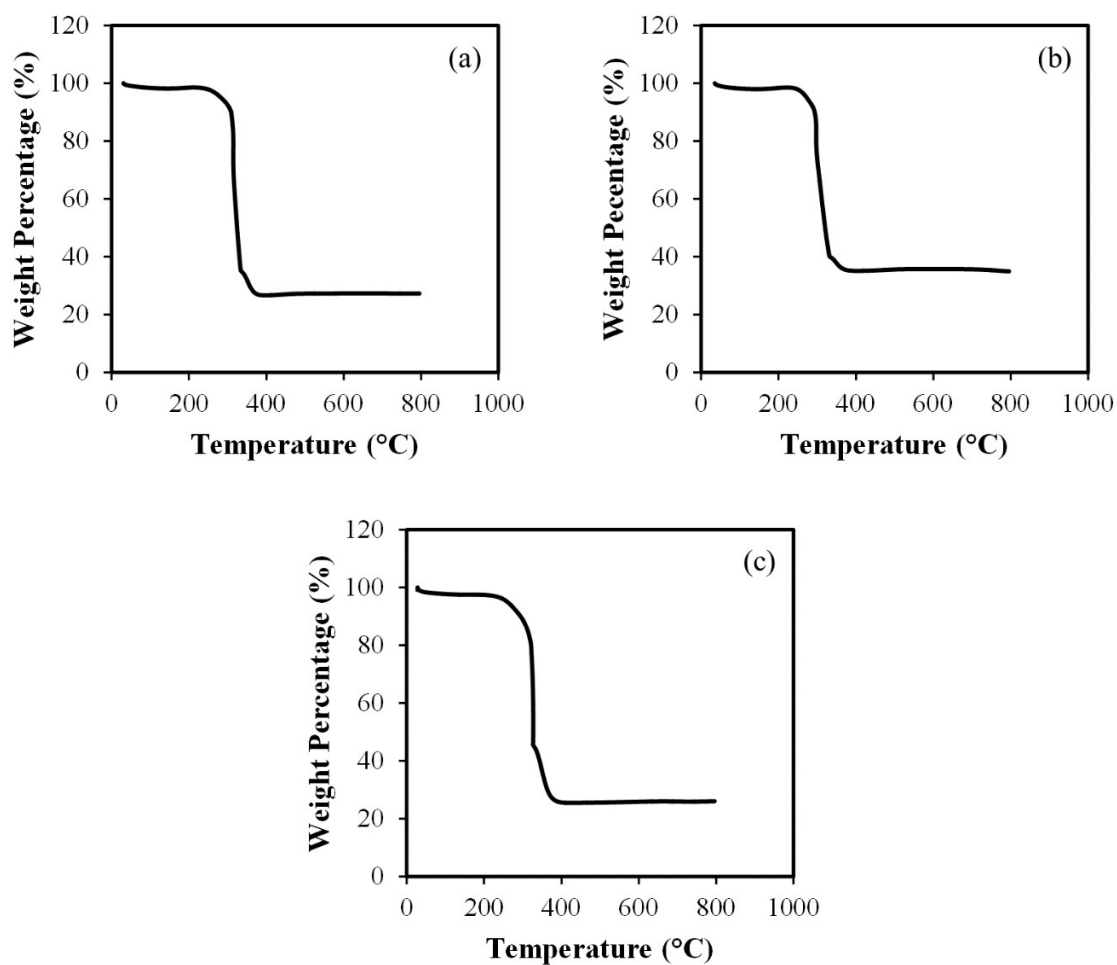


Figure 49: TGA graphs of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

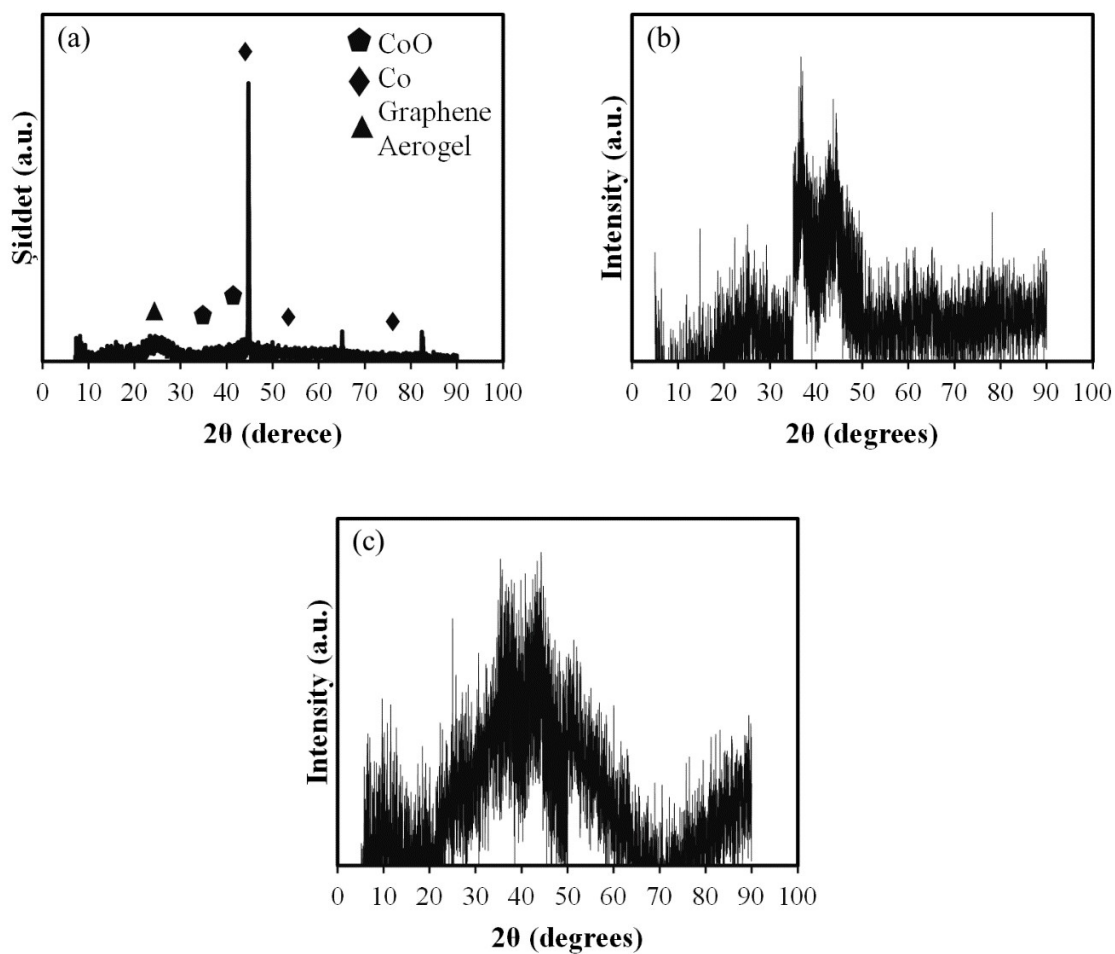


Figure 50: XRD patterns of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

Table 14: Cobalt loading ratios according to the samples' impregnation solution concentration, and average crystal size of cobalt according to Scherrer Equation

Impregnation Solution Concentration (mol/L)	Alkali Metal, and Impregnation Solution Concentration (mmol/L)	Mass Percentage of Cobalt Oxide (Co_3O_4) (%)	Mass Percentage of Cobalt (%)	Average Cobalt Crystal Size (nm)
0.1	K, 5.3	26.05	18.84	15.42
0.1	Na, 5.3	34.93	25.27	58.99
0.1	Li, 5.3	27.26	19.72	50.74

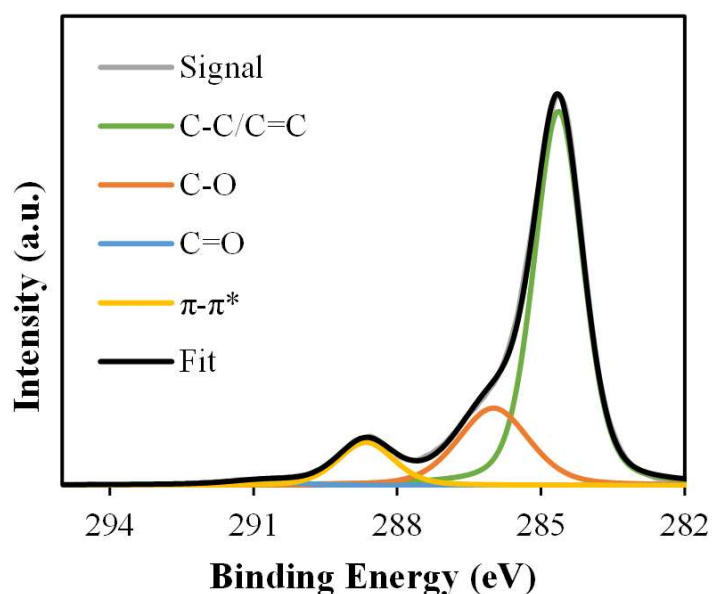


Figure 51: XPS C1s spectrum of lithium added cobalt loaded graphene aerogel

Lithium added cobalt loaded catalyst's XPS C1s spectrum is given in Figure 51. The spectrum is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen

double bonds, and π - π^* transition, respectively. When compared with thermally reduced graphene oxide, peak corresponding carbon-oxygen double bonds is slightly elevated. When compared with the lithium added iron catalyst the spectra are similar in terms of increase in the peak. Lithium addition may affect the reduction amount in the graphene aerogel. Li1s spectrum is also investigated. However, no indication of lithium was found via XPS.

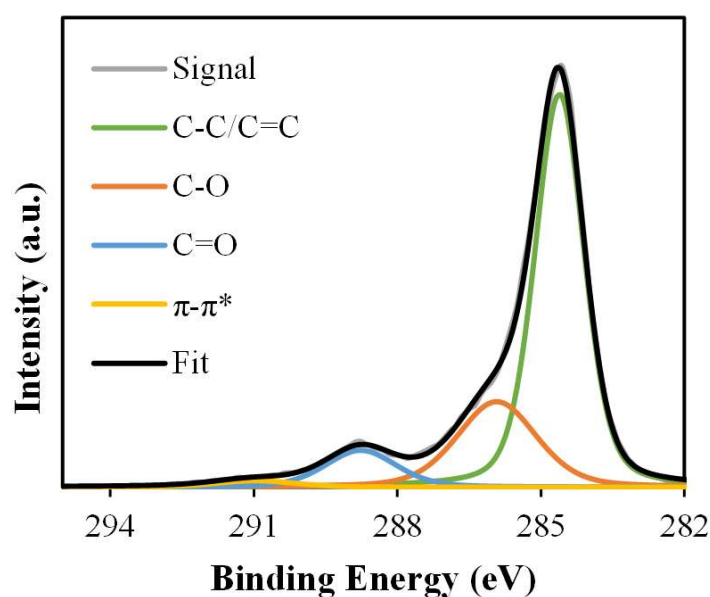


Figure 52: XPS C1s spectrum of sodium added cobalt loaded graphene aerogel

Sodium added cobalt loaded graphene aerogel's XPS C1s spectrum is given in Figure 52. Signals deconvoluted to four peaks corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and π - π^* transition. In lithium added cobalt loaded catalyst an increase of carbon-oxygen double bond amount is detected when compared to thermally reduced graphene aerogel. The same peak's intensity in sodium added cobalt loaded catalyst is increased. Sodium added iron-loaded catalyst's XPS C1s spectrum does not show such an increase in the peak. Na1s spectrum of the catalyst is investigated, no signal is obtained.

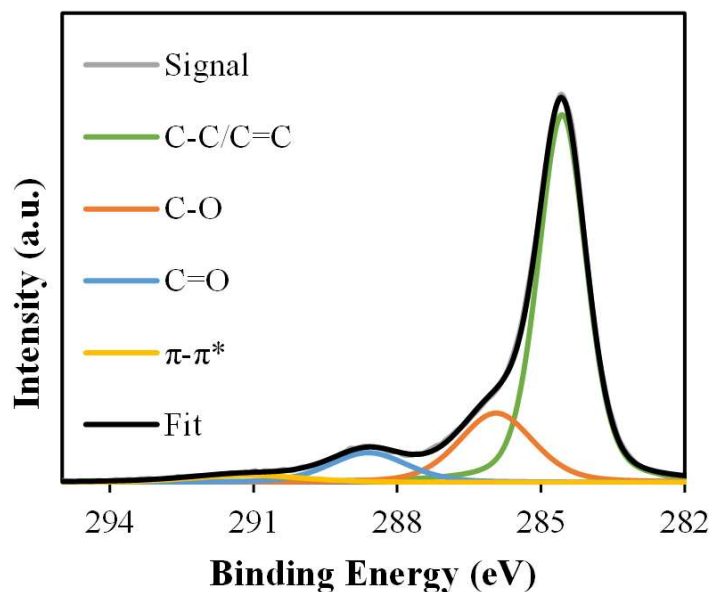


Figure 53: XPS C1s spectrum of potassium added cobalt loaded graphene aerogel

Potassium added cobalt loaded graphene aerogel's XPS C1s spectrum is given in Figure 53. Spectrum is deconvoluted to four peaks similar to other catalysts. The carbon-oxygen double bond signal is elevated when compared to thermally reduced graphene aerogel. This increase is observed in lithium, and sodium added cobalt loaded catalysts. K2p spectrum is investigated, no signal indicating potassium presence detected. Raman is used for analyzing defect amounts. I_D/I_G ratios can be calculated from Raman peaks which are previously deconvoluted. The ratios show that they are similar to each other, only cobalt loaded catalysts, and graphene aerogel. This shows that alkali metal and cobalt addition to graphene aerogels do not affect the defect amount.

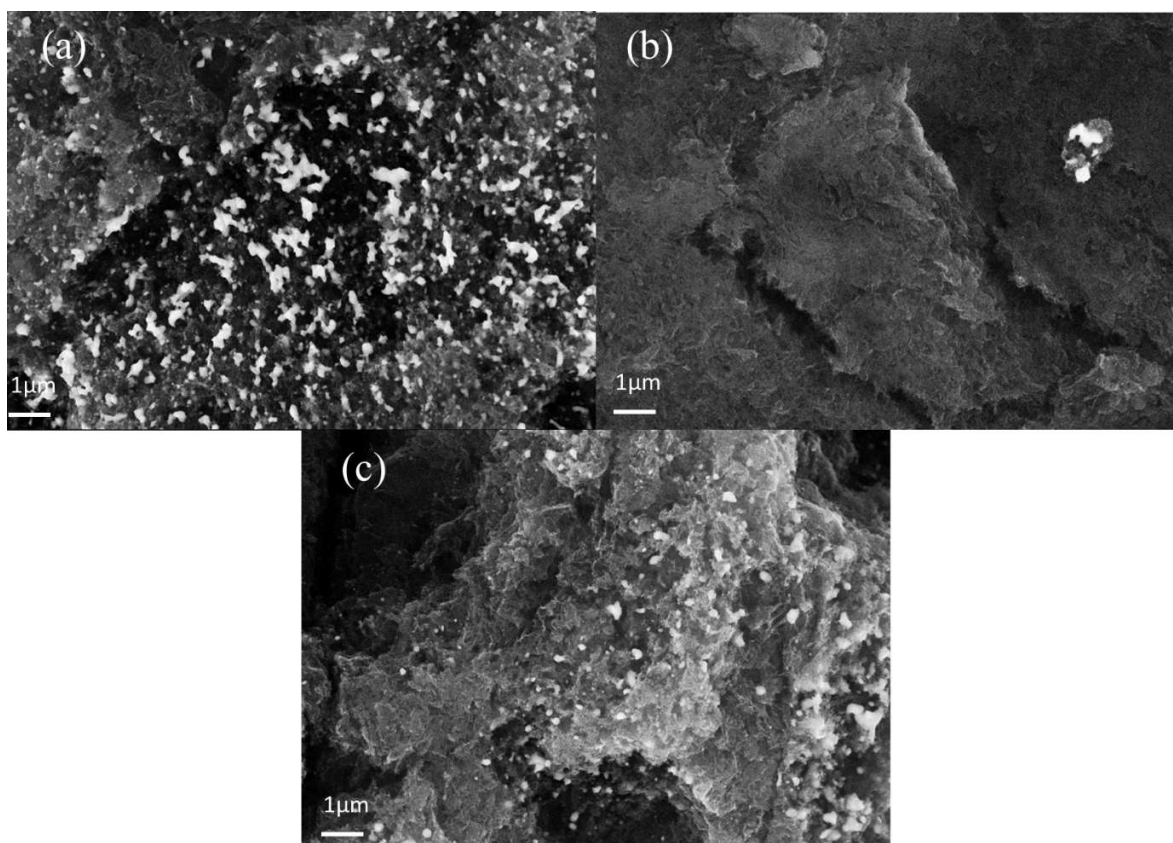


Figure 54: SEM images of lithium (a), sodium (b), and potassium (c) added cobalt-loaded graphene aerogels. In Figure 54 SEM images of alkali metal added cobalt-loaded graphene aerogels. The porous structure did not affect by the alkali metal addition. Bright spots on the images are the cobalt-loaded sites. Through alkali metals, lithium does not generate good contrast in SEM images⁹¹. No other metal structure is detected in the SEM.

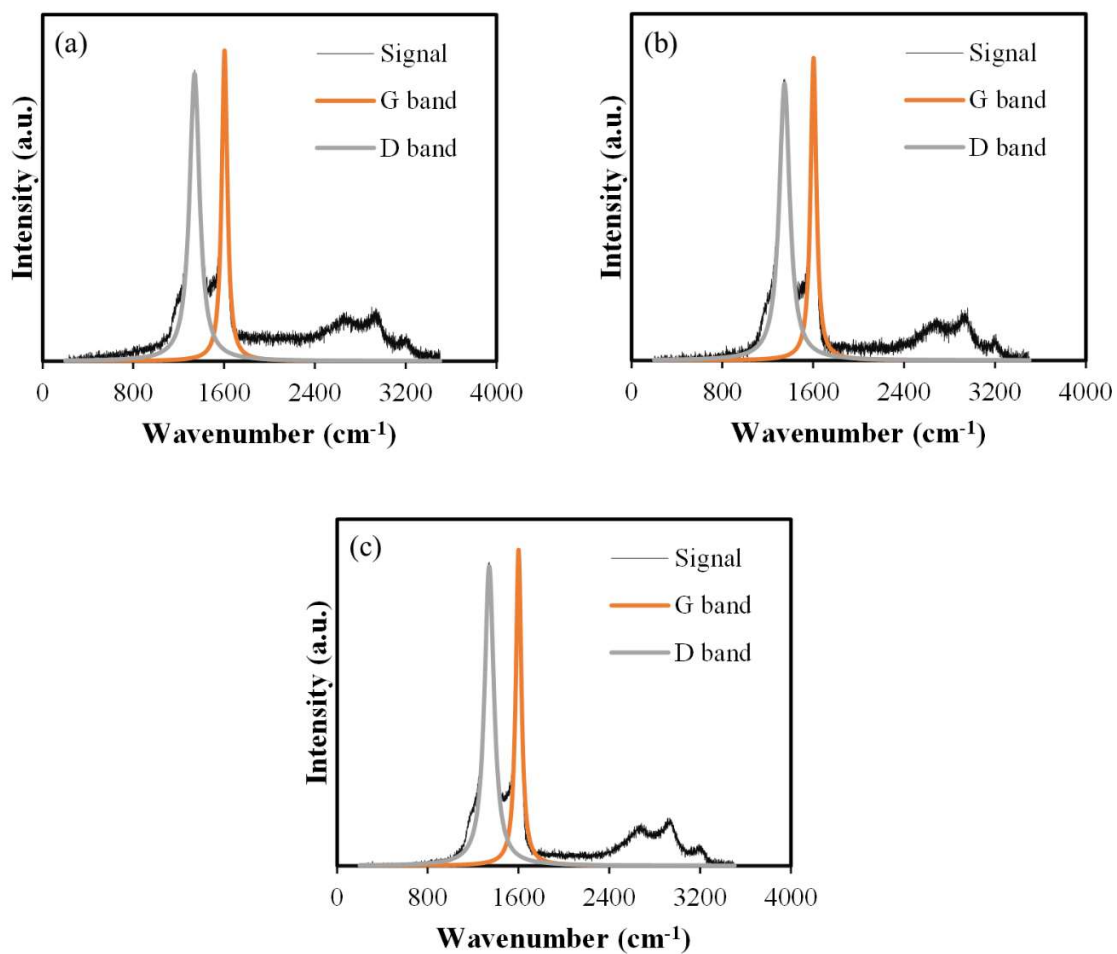


Figure 55: Raman spectra of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

Table 15: I_D/I_G ratios of alkali metal added cobalt loaded graphene aerogels

Impregnation Solution Concentration (mol/L)	Alkali Metal, and Impregnation Solution Concentration (mmol/L)	Mass Percentage of Cobalt (%)	I_D/I_G
0.1	K, 5.3	18.84	0.96
0.1	Na, 5.3	25.27	0.91
0.1	Li, 5.3	19.72	0.93

4.3.3. Catalytic Performance of Cobalt Loaded Graphene Aerogels for Ammonia Decomposition Reaction

Ammonia conversion performance of the prepared catalysts is evaluated via gas chromatograph. In low conversion range, Arrhenius plots are generated to calculate the activation energy of the reaction with the catalyst. Low conversion is reached between 400, and 440 °C. Catalysts' which loaded with cobalt in 0.1, 0.075, and 0.05 M solutions Arrhenius plots are drawn under 100000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity, whereas catalyst's cobalt loaded in 0.0125 M impregnation solution plot is drawn under 200000 NH₃ g_{cat}⁻¹ h⁻¹ space velocity, and catalyst's cobalt loaded in 0.0025 M Arrhenius plot is drawn under 600000 NH₃ g_{cat}⁻¹ h⁻¹ space velocity. Activation energy is deducted from the slope of the plots. Arrhenius plots are presented in Figure 56, and activation energy values are presented in Table 16.

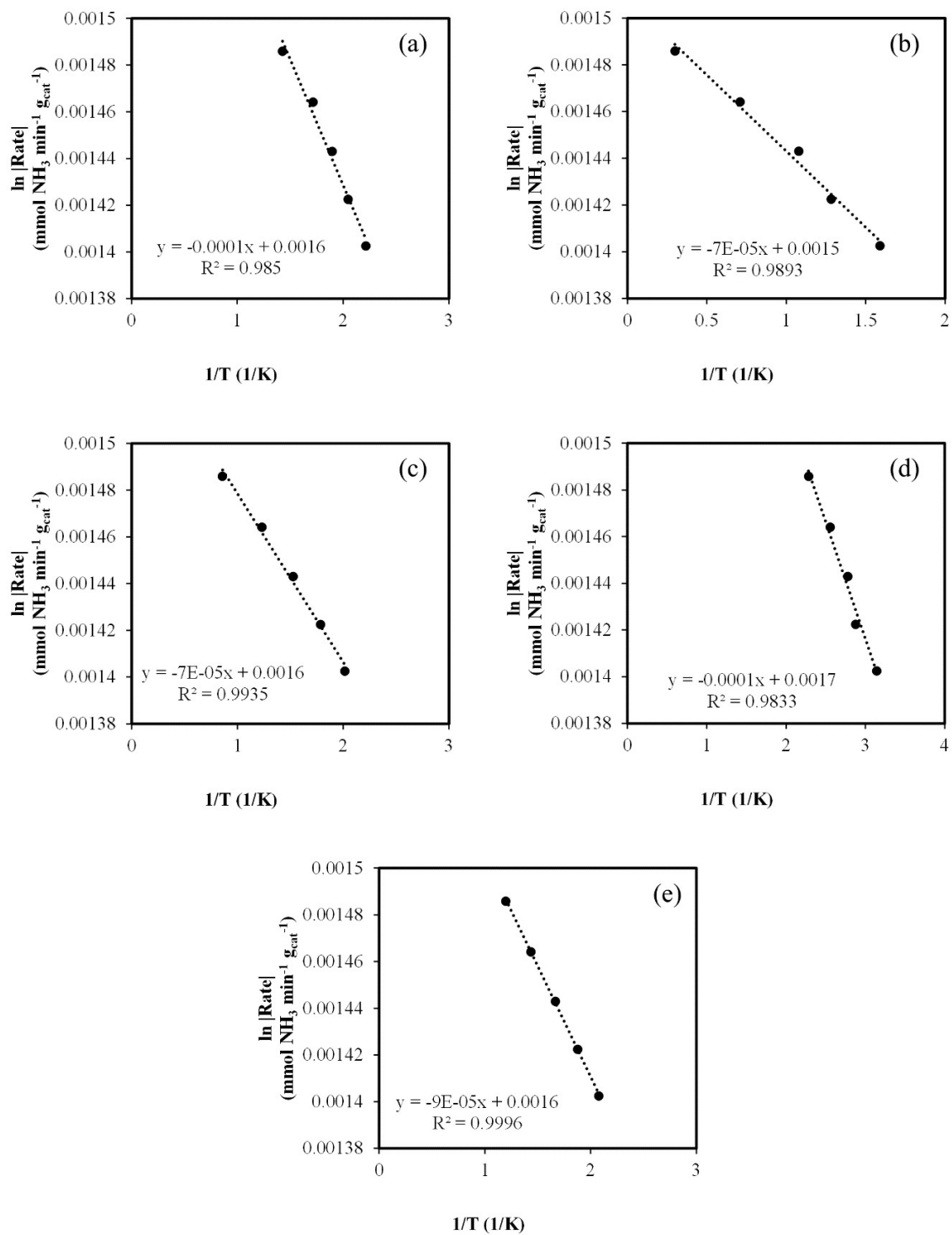


Figure 56: Arrhenius plots of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

Table 16: Activation energy values of ammonia decomposition with cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M, 0.075 M, 0.05 M, 0.0125 M , and 0.0025 M

Impregnation Solution	Mass Percentage	Activation
Concentration (mol/L)	of Cobalt (%)	Energy (kJ/mol)
0.0025	3.19	87.91
0.0125	7.98	81.44
0.05	11.78	114.4
0.075	17.28	126.1
0.01	20.11	76.13

Ammonia conversion performances of the catalysts are measured under pure ammonia flow. Measurements are taken in different temperatures, and space velocities. In Figure 57 ammonia conversion percentages of samples in a temperature gradient are given. Temperature and space velocity are the factors affecting the catalysts' performance. An increase in temperature and a decrease in space velocity yields an increase of the ammonia conversion. The highest ammonia conversion measured with a cobalt loaded catalyst is 87.7% achieved by 20.11% cobalt loaded catalyst at 600 °C under 10000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. Other catalysts also performed similar ammonia conversions under the same conditions. Hydrogen production rates of the catalysts are also calculated from the ammonia consumption rate. Per mass, 3.19% cobalt loaded catalyst achieved the highest hydrogen production rate with 124.6 mmol H₂ g_{cat}⁻¹ min⁻¹. TOF values are also calculated for cobalt loaded catalysts. The average crystal size of the loaded cobalt is found by the Scherrer equation. Highest TOF is achieved by 3.19% cobalt loaded catalyst. At 600 °C under 400000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity catalyst achieved 336.4 s⁻¹ turnover frequency. Hydrogen

production rate and TOF values are visualized in Figure 58, and Figure 59 respectively. Ammonia conversion percentages, hydrogen production rates, and TOF at 600 °C is presented in Table 17. In the literature, cobalt catalysts are not used as much as iron catalysts. A summary of the literature is given in Table 18. Ammonia conversion values of cobalt loaded graphene aerogels achieved more than any other cobalt catalyst in the literature. However, the instability of the catalyst needs improvement.



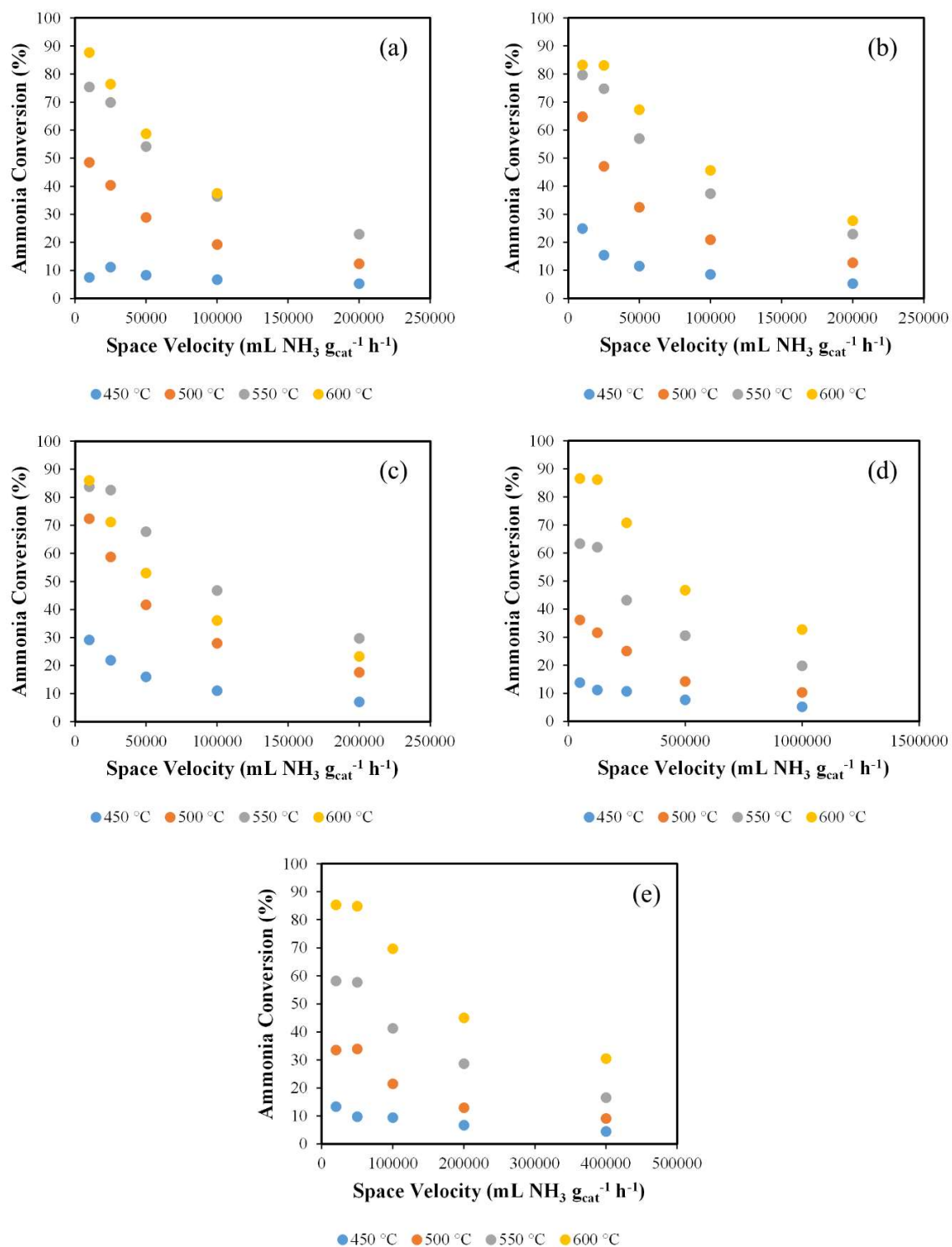


Figure 57: Ammonia conversion percentages according to different space velocity, and temperatures of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

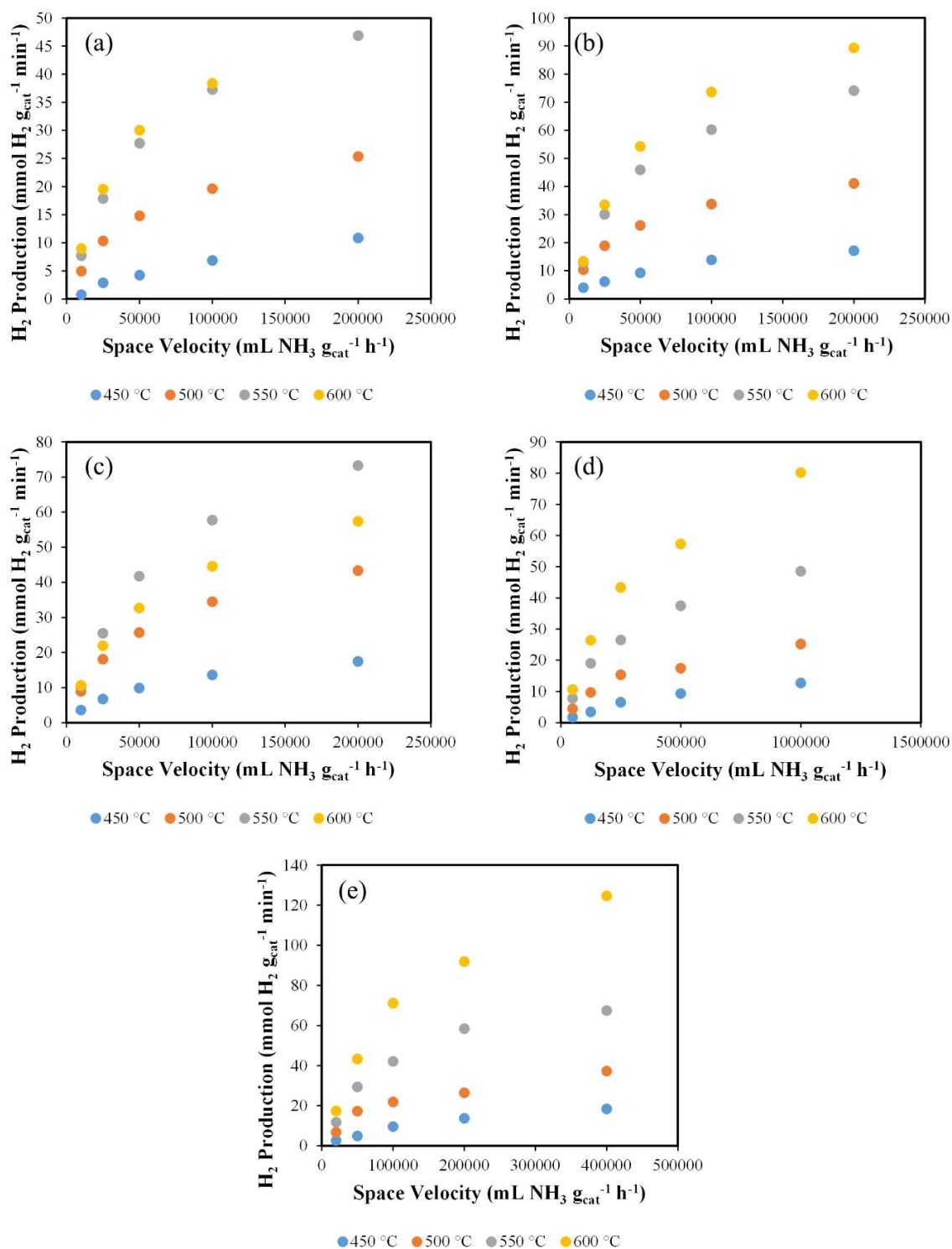


Figure 58: H₂ production rates according to different space velocity, and temperatures of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

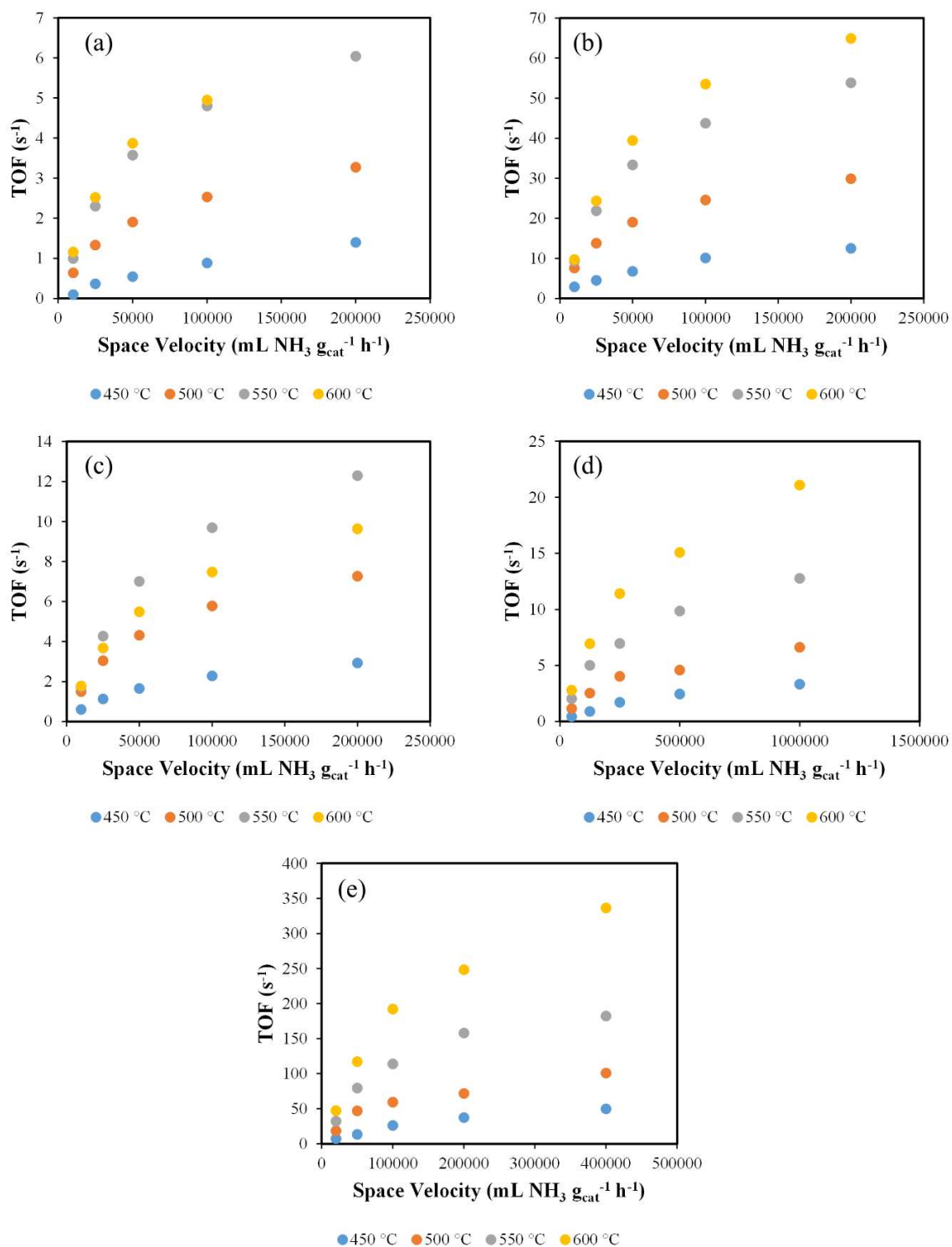


Figure 59: Turnover frequencies according to different space velocity, and temperatures of cobalt loaded graphene aerogels with different impregnation solution concentration, 0.1 M (a), 0.075 M (b), 0.05 M (c), 0.0125 M (d), and 0.0025 M (e)

Table 17: Ammonia conversion percentages, hydrogen production rates, and TOF values of samples with different cobalt loading ratio at 600 °C

Iron Loading (%)	Space velocity (mL NH₃ g_{cat}⁻¹ h⁻¹)	Ammonia conversion (%)	H2 Production Rate (mmol H₂ g_{cat}⁻¹ min⁻¹)	TOF (s⁻¹)
20.11	100000	37.5	38.4	4.9
	50000	58.7	30.0	3.9
	25000	76.4	19.5	2.5
	10000	87.7	9.0	1.2
17.28	200000	27.7	89.4	64.9
	100000	45.7	73.7	53.5
	50000	67.3	54.3	39.4
	25000	83.1	33.5	24.3
	10000	83.3	13.4	9.8
11.78	200000	23.3	57.4	9.6
	100000	36.1	44.6	7.5
	50000	53	32.7	5.5
	25000	71.2	22	3.7
	10000	86.1	10.6	1.8

7.98	1000000	32.7	80.2	21.1
	500000	46.7	57.3	15.1
	250000	70.7	43.4	11.4
	125000	86.1	26.4	6.9
	50000	86.5	10.6	2.8
3.19	400000	30.5	124.6	336.4
	200000	45	92	248.3
	100000	69.7	71.2	192.1
	50000	84.8	43.4	117
	20000	85.3	17.4	47

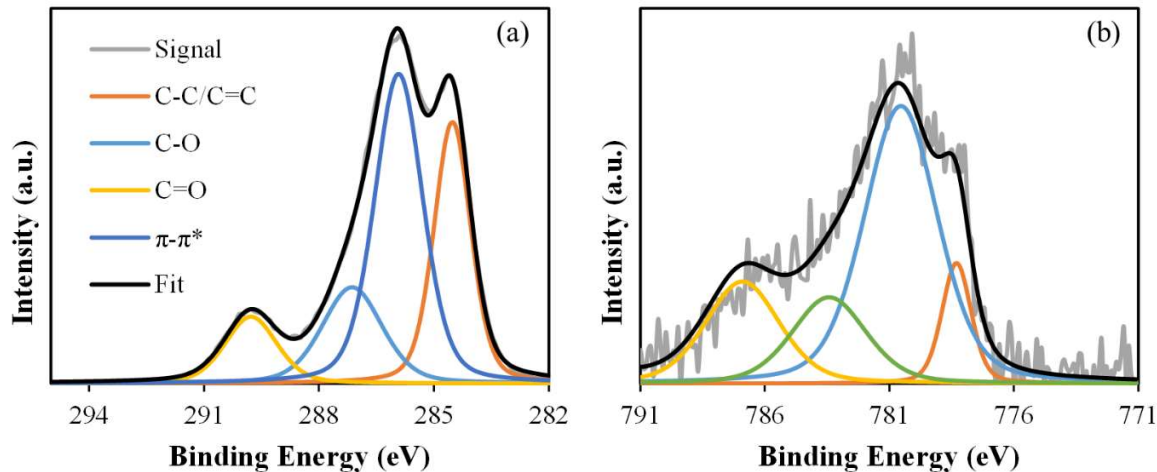


Figure 60: XPS C1s (a), and Co2p_{3/2} (b) spectra of cobalt loaded graphene aerogel after ammonia decomposition reaction

In Figure 60 (a), the XPS C1s spectrum is given. The signal is deconvoluted to four peaks at 284.5, 286.5, 288.0, and 291.1 eV corresponding to carbon-carbon double, and single bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and $\pi-\pi^*$ transition respectively.

A sharp increase in the carbon-oxygen single bond intensity relative to thermally reduced graphene aerogel is unexpected, which means the sample is not reduced enough. In Figure 60 (b) cobalt spectrum deconvoluted to four peaks. The peak at 778.3 eV is matching with the metallic cobalt peak whereas other peaks are oxidized cobalt's peaks. N1s spectrum is scanned, no signal indicating nitrogen found in the sample.

During the performance measurements of the cobalt loaded graphene aerogels data are collected in the peak ammonia conversion instead of after its stabilization. This is because of the instability of the ammonia conversion with cobalt loaded catalysts. The conversion percentages decrease even during the data collection.

Cobalt is one of the known active metals for the ammonia decomposition reaction. Figure 2 shows that the cobalt catalyst has a similar rate constant with iron and its energy requirement is less for the reaction. When these are considered the catalytic activity of cobalt catalysts are expected to be higher than iron catalysts. However, the measurements are contradicted with the expectations, cobalt catalysts converted slightly less than iron catalysts. Besides the conversion rates, another important parameter for a catalyst is stability. In minutes span, cobalt catalysts' ammonia conversion rates are showed sharp decreases. The reason behind the instability may be the oxygen-containing groups that are not removed by the thermal reduction. These groups are detected via XPS before and after the reaction. The presence of the carbon-oxygen bond in the support material would decrease the electrical conductivity of the support material. The electrical conductivity of the support material increases the electron mobility near active sites which helps reaction to take place. Because of these carbon-oxygen bonds electron movement may be reduced.

According to the reaction rate, cobalt has the potential to be a cheaper option for ruthenium catalysts. However, as a catalyst support graphene aerogels are not suitable for unleashing the potential of cobalt catalysts.

Table 18: A performance summary of cobalt catalyst on various support materials

Sample Name	Reaction Temperature (°C)	Ammonia Conversion (%)	Space velocity (mL NH ₃ g _{cat} ⁻¹ h ⁻¹)	Activation Energy (kJ/mol)	Reference
%7Co/Ax21	500	70	5200	88.74	21
Co/CNT	500	51.9	12000	-	115
%5Co/MgOLa ₂ O ₃	500	85	6000	67.1	60
Co/Fe support	550	24	-	-	116

4.3.4. Catalytic Performance of Alkali Metal Added Cobalt Loaded Graphene Aerogels for Ammonia Decomposition Reaction

Alkali metal addition is made to the cobalt loaded catalysts with the aim of increasing the ammonia decomposition performance. In the case of the instability of the cobalt catalyst, alkali metal addition is also controlled for stability. Arrhenius plots are drawn with the data from the low conversion range. The low conversion range is between 400, and 440 °C with the flow of 100000 mL NH₃ g_{cat}⁻¹ h⁻¹. Arrhenius plots are presented in Figure 61, and calculated activation energy values are listed in Table 19.

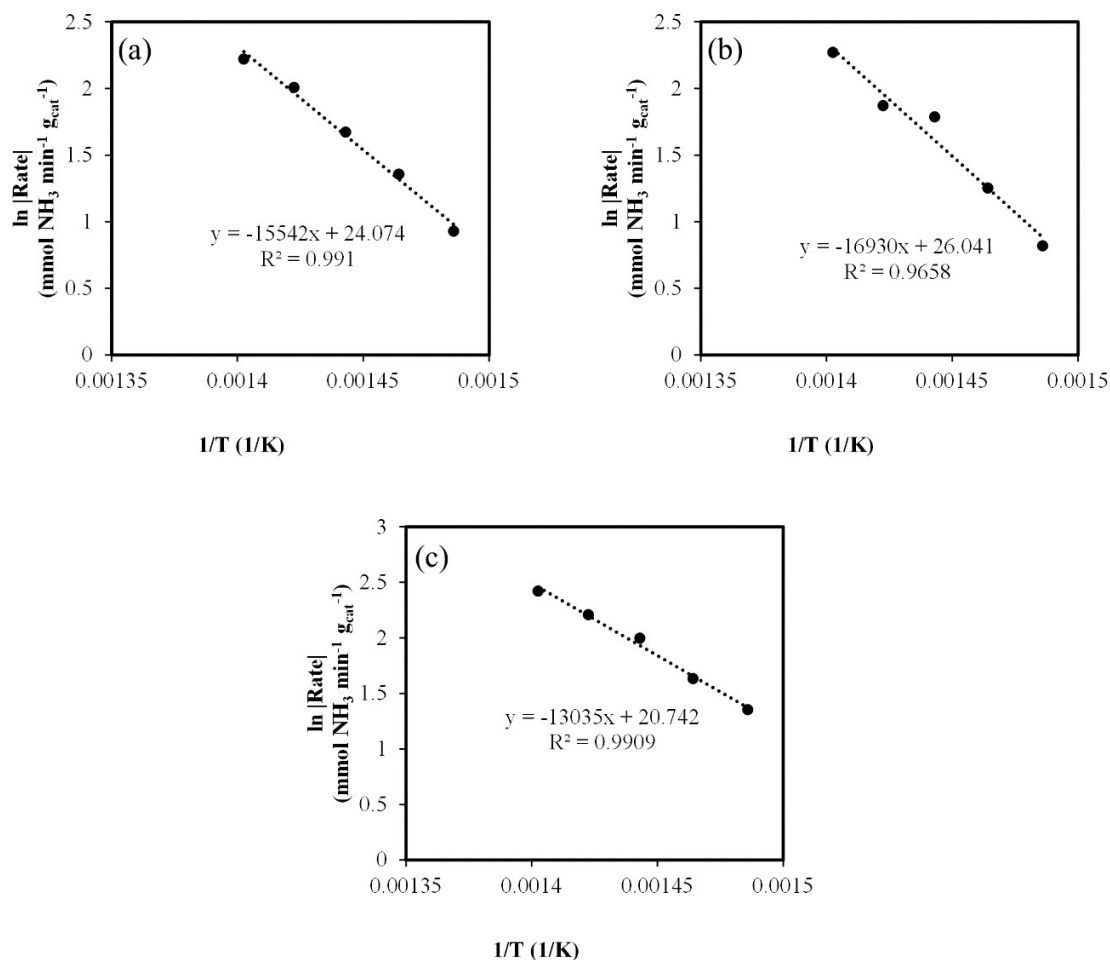


Figure 61: Arrhenius plot of lithium, sodium, and potassium added cobalt loaded graphene aerogels

Table 19: Different alkali metal additive's activation energies according to Arrhenius plots

Impregnation Solution	Alkali Metal, and	Mass	Activation
Concentration (mol/L)	Impregnation Solution	Percentage of	Energy
	Concentration (mmol/L)	Cobalt (%)	(kJ/mol)
0.1	K, 5.3	18.84	108.3
0.1	Na, 5.3	25.27	140.7
0.1	Li, 5.3	19.72	129.2

Ammonia decomposition, hydrogen production rate, and TOF values are given in Figure 62, Figure 63, and Figure 64 respectively. Also, the summary of these values obtained at 600 °C is listed in Table 20. Contrary to iron-loaded catalysts lithium added cobalt loaded catalyst is performed better. At 550 °C under 10000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity lithium added cobalt loaded catalyst reached to 100% ammonia conversion. The same sample also reached 100% ammonia conversion at 600 °C under 25000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. The sample reached 67.3 mmol H₂ g_{cat}⁻¹ min⁻¹ hydrogen production rate with a TOF of 16.1 s⁻¹. Because of the increase in the performance stability of the lithium added catalyst is tested. On the other hand, sodium added catalysts are performed significantly less than cobalt loaded

catalyst. Potassium added catalyst converted slightly less ammonia than only cobalt loaded catalyst.

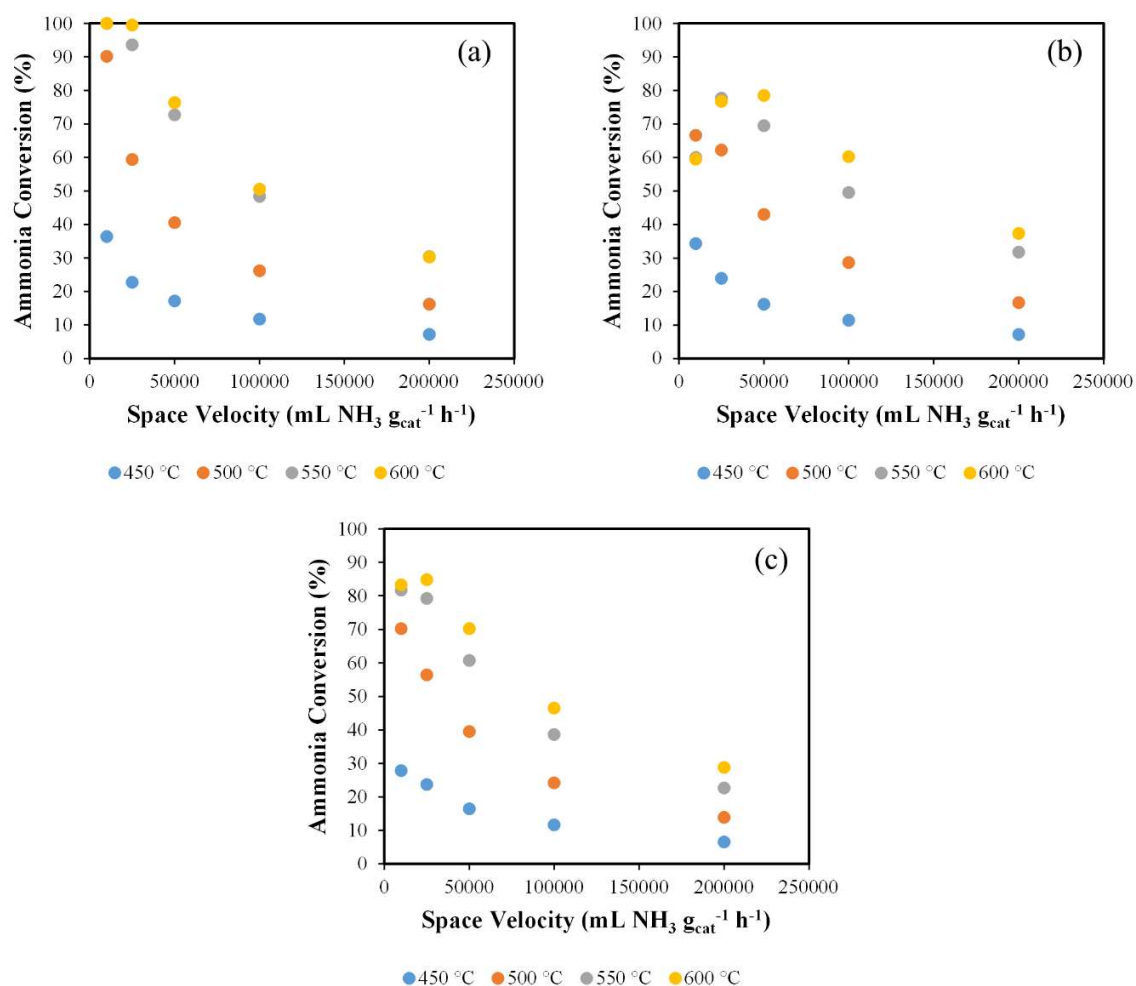


Figure 62: Ammonia conversion amounts according to different space velocity, and temperatures of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

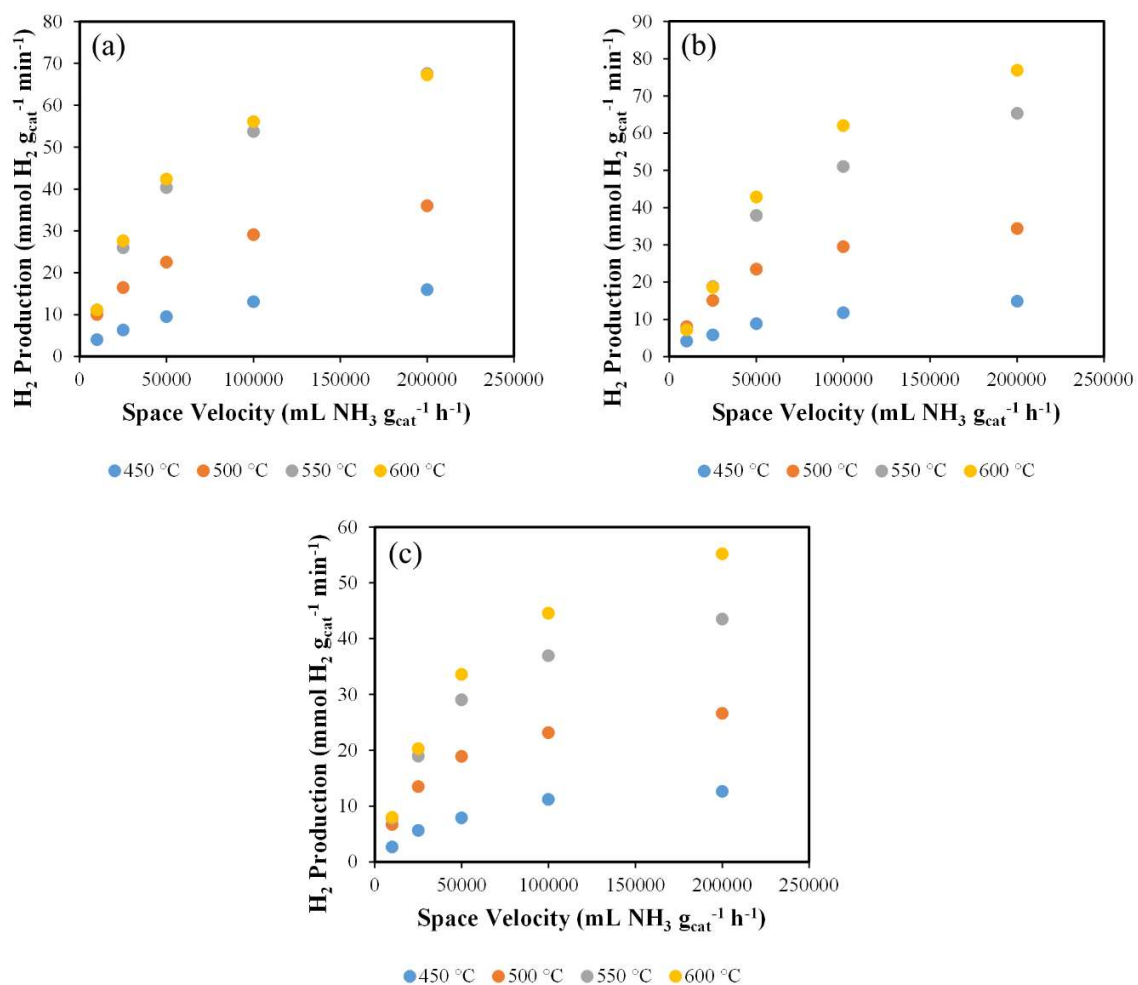


Figure 63: Hydrogen production rates according to different space velocity, and temperatures of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

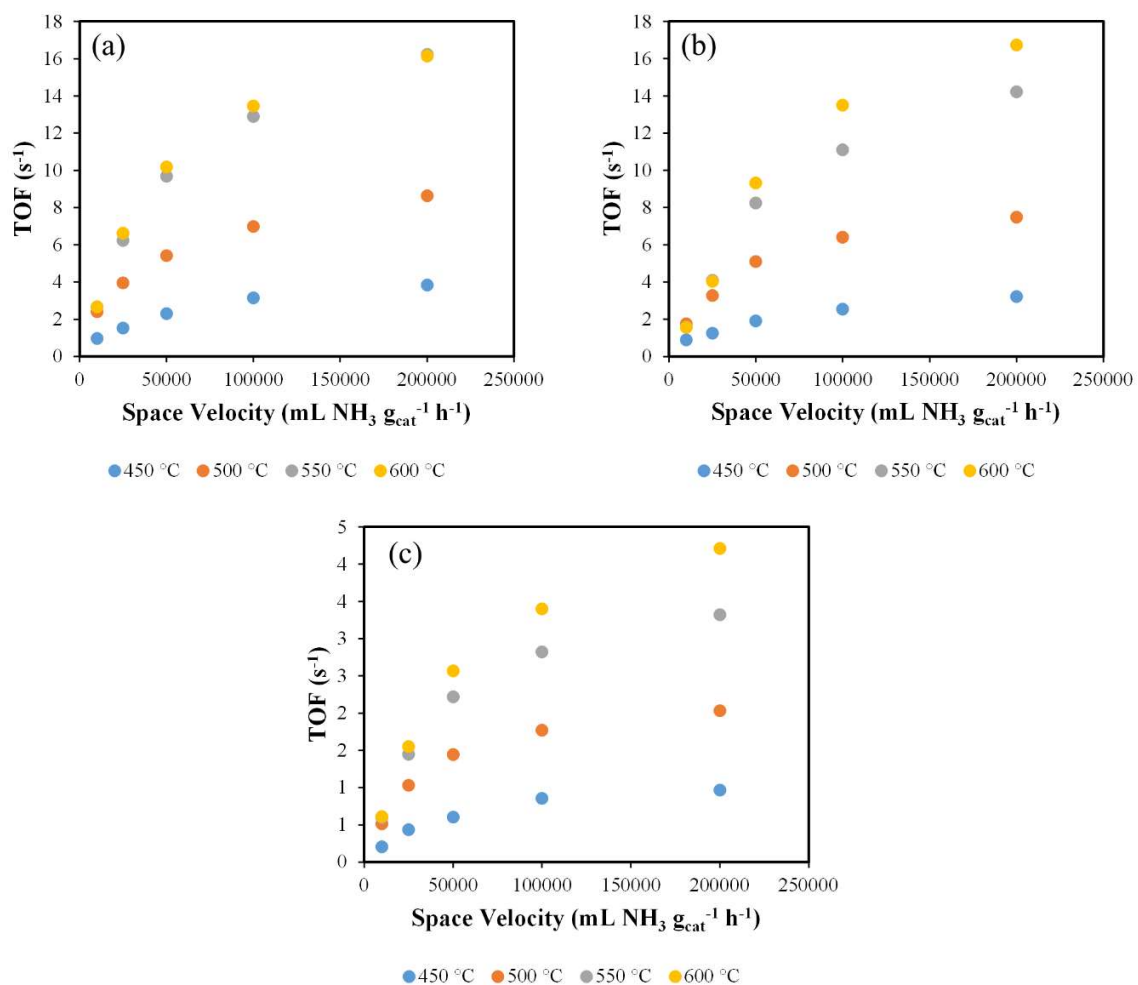


Figure 64: Turnover frequencies according to different space velocity, and temperatures of alkali metal added cobalt loaded graphene aerogels, Li (a), Na (b), and K (c)

Table 20: Ammonia conversion percentages, hydrogen production rates, and TOF values of samples with different alkali metal addition at 600 °C

Sample	Space velocity (mL NH₃ g_{cat}⁻¹ h⁻¹)	Ammonia conversion (%)	H₂ Production Rate (mmol H₂ g_{cat}⁻¹ min⁻¹)	TOF (s⁻¹)
Co- Li/GA	200000	30.3	67.3	16.1
	100000	50.5	56.1	13.5
	50000	76.4	42.4	10.2
	25000	99.5	27.6	6.6
	10000	100	11.1	2.7
Co- Na/GA	200000	37.3	76.9	16.7
	100000	60.2	62	13.5
	50000	78.5	42.8	9.3
	25000	76.7	18.6	4
	10000	59.5	7.2	1.6
Co- K/GA	200000	28.8	55.2	4.2
	100000	46.5	44.5	3.4
	50000	70.2	33.6	2.6
	25000	84.8	20.3	1.5
	10000	83.3	8	0.6

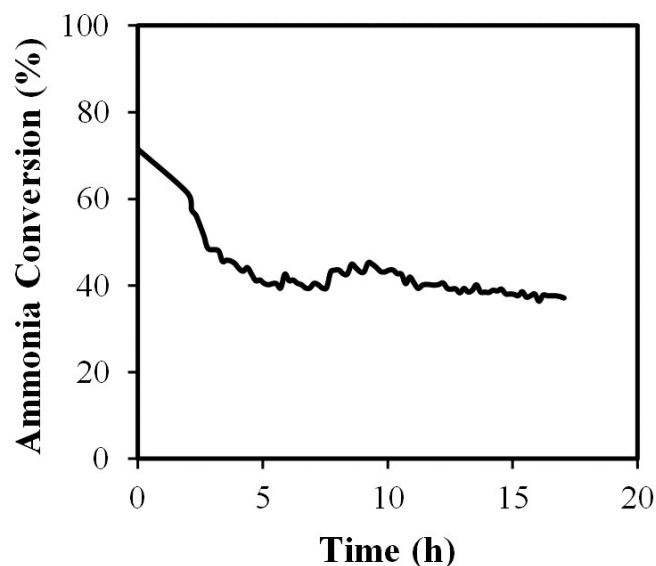


Figure 65: Lithium added cobalt loaded graphene aerogel's ammonia conversion for 16 hours

In Figure 65, lithium added cobalt loaded graphene aerogel's ammonia conversion over time is investigated. After 16 hours at 600 °C, under 25000 mL $\text{NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ space velocity ammonia conversion percentage dropped from over 70% to below 40%. The instability of the cobalt catalyst continued with the lithium addition. The sharp decrease in ammonia conversion over time shows the instability of the catalyst.

In the literature, only one study used alkali metals to promote the ammonia decomposition ability of the catalyst. Torrente-Murciano et al. used 7% loaded Ax-21 carbon as ammonia decomposition catalyst²¹. Alkali metal addition in this work is cesium. 1:1 molar ratio of cesium and cobalt is loaded on Ax-21 carbon. At 500 °C, under 5200 mL $\text{NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ space velocity only cobalt-containing catalyst converted 70 percent of the ammonia whereas, cesium added sample converted 30% of the ammonia. Alkali metal addition to a cobalt catalyst decreased the performance in their study similar to this work.

Similar to the cobalt catalysts part of the carbon-oxygen bonds have remained in the alkali promoted cobalt catalysts after thermal reduction. The reason behind the low conversion rates may be the presence of the carbon-oxygen bonds. Na and K promotion, parallel to the alkali promoted iron catalysts, resulted in a decrease in ammonia decomposition rates. However, Li promoted cobalt catalyst's ammonia decomposition rate is higher than the cobalt catalyst. Even though Li promotion increased the decomposition rate, Li promotion did not help the instability of the cobalt catalyst.

4.4. Conclusion

Graphene aerogels are loaded with cobalt particles via the impregnation method. The concentration of the impregnation solution monitored the loading ratios. The thermal reduction is performed and confirmed with characterization methods. Cobalt loading ratios are calculated with the help of TGA, and XRD. Morphology and defects are investigated via SEM and Raman. Alkali metal addition is performed to increase the ammonia conversion of the catalysts. However, the presence of the alkali metals on the catalyst could not be detected. Low concentrations may affect the results of the detection of alkali metals. The catalytic performance of the catalysts is measured with gas chromatograph. The highest ammonia conversion with cobalt loaded graphene aerogel is measured as 87.7% at 600 °C, under 10000 mL NH₃ g_{cat}⁻¹ h⁻¹ space velocity. Sodium and potassium additions negatively affected the ammonia conversion amount of the catalyst. Lithium added catalyst converted more ammonia than only cobalt-containing catalysts. Instability of the cobalt catalysts continued with the alkali metal addition.

Chapter 5: Conclusions and Further Work

Because of the high, and increasing demand for energy alongside harmfulness, and limited supply of carbon-based fuels, the pursuit of alternative, sustainable, clean, and efficient fuel started. One of the candidates of the future's fuel is hydrogen because of its high energy density, and clean nature. When used as fuel hydrogen's only waste is water. The main energy sources today are carbon-based fossil fuels. CO_x emission caused by fossil fuels causes air pollution, and increase the rate of global warming. Storage and production of hydrogen need to be efficient to replace fossil fuels. Ammonia is one of the hydrogen-containing molecules which consists of 17.7% hydrogen by mass. Hydrogen storage in ammonia is one of the propositions for solving the storage, and logistics issue of hydrogen. Because of the high temperature, and catalyst requirements of the ammonia decomposition reaction, an efficient catalyst needs to be designed. For this reaction, precious noble metals, and inexpensive transition metals are used. In order to decrease the cost of the catalysts ways to increase the activity of inexpensive catalysts were searched. Catalyst support materials help to increase catalytic activity via increasing surface area, and electrical conductivity. In this thesis, high surface area graphene aerogels are synthesized from the graphene oxide solution. Graphene oxide is obtained via oxidation of graphite via modified Hummers' method and ultrasound-assisted exfoliation. Hydrogels resulting from a hydrothermal reaction of the graphene oxide is dried with supercritical CO₂ after solvent exchange. This drying method decreased the loss of surface area during drying.

Iron is one of the most studied ammonia decomposition catalysts. However, to reach the activity of more expensive metals such as ruthenium, graphene aerogel supported iron catalysts' catalytic performances were investigated. Cobalt is another metal that showed

catalytic activity for the reaction. Because of the relatively low catalytic performance, in the literature, there are fewer studies on it. Iron and cobalt were loaded on the aerogels via the impregnation method. The thermal reduction method is used to reduce catalysts. Iron catalysts achieved 100% ammonia conversion at 600 °C. Alkali metal addition is made to increase the conversion. However, alkali metal addition decreased the conversion. Cobalt catalysts converted as high as 87.7% of ammonia at 600 °C. Cobalt catalysts had an unstable conversion that showed sharp decreases in conversion. Lithium addition to cobalt catalyst significantly increased the conversion. However, alkali metal addition did not solve the instability.

Because of the Covid-19 pandemic, the work on this thesis is delayed and some of the work remain uncompleted. To make this thesis more complete, additional work needs to be done. The necessary additional work are listed below:

- At the beginning of the study, for all different metal loading alkali metal addition is aimed and alkali metal additions are started with a random metal loading for iron samples instead of the best performing one. The alkali metal addition to better performing iron catalyst for catalytic activity measurements is necessary for this work.
- There is an inconsistency between the metal loadings of iron catalysts, which needs to be further confirmed with TGA by increasing the sample size and analyze whether these values are outliers.
- Because of the time restrictions, better performing iron catalysts are prioritized over cobalt catalysts and some measurements or characterizations of cobalt

catalysts are lacking such as stability measurements of cobalt catalysts or after reaction XRD of cobalt catalysts.



BIBLIOGRAPHY

1. Schüth F, Palkovits R, Schlögl R, Su DS. Ammonia as a possible element in an energy infrastructure: Catalysts for ammonia decomposition. *Energy and Environmental Science*. 2012;5(4):6278–6289. doi:10.1039/c2ee02865d
2. Bell TE, Torrente-Murciano L. H₂ Production via Ammonia Decomposition Using Non-Noble Metal Catalysts: A Review. *Topics in Catalysis*. 2016;59(15–16):1438–1457. doi:10.1007/s11244-016-0653-4
3. Kurtoğlu SF, Sarp S, Yılmaz Akkaya C, Yağcı B, Motallebzadeh A, Soyer-Uzun S, Uzun A. CO_x-free hydrogen production from ammonia decomposition over sepiolite-supported nickel catalysts. *International Journal of Hydrogen Energy*. 2018;43(21):9954–9968. doi:10.1016/j.ijhydene.2018.04.057
4. Abe JO, Popoola API, Ajenifuja E, Popoola OM. Hydrogen energy, economy and storage: Review and recommendation. *International Journal of Hydrogen Energy*. 2019;44(29):15072–15086. <https://doi.org/10.1016/j.ijhydene.2019.04.068>. doi:10.1016/j.ijhydene.2019.04.068
5. Rusman NAA, Dahari M. A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. *International Journal of Hydrogen Energy*. 2016;41(28):12108–12126. <http://dx.doi.org/10.1016/j.ijhydene.2016.05.244>. doi:10.1016/j.ijhydene.2016.05.244
6. Midilli A, Ay M, Dincer I, Rosen MA. On hydrogen and hydrogen energy strategies I: Current status and needs. *Renewable and Sustainable Energy Reviews*. 2005;9(3):255–271. doi:10.1016/j.rser.2004.05.003

7. Iordache I, Schitea D, Gheorghe A V., Iordache M. Hydrogen underground storage in Romania, potential directions of development, stakeholders and general aspects. *International Journal of Hydrogen Energy*. 2014;39(21):11071–11081. <http://dx.doi.org/10.1016/j.ijhydene.2014.05.067>. doi:10.1016/j.ijhydene.2014.05.067
8. Hwang HT, Varma A. Hydrogen storage for fuel cell vehicles. *Current Opinion in Chemical Engineering*. 2014;5:42–48. <http://dx.doi.org/10.1016/j.coche.2014.04.004>. doi:10.1016/j.coche.2014.04.004
9. Webb CJ. A review of catalyst-enhanced magnesium hydride as a hydrogen storage material. *Journal of Physics and Chemistry of Solids*. 2015;84(1):96–106. <http://dx.doi.org/10.1016/j.jpcs.2014.06.014>. doi:10.1016/j.jpcs.2014.06.014
10. Eftekhari A, Fang B. Electrochemical hydrogen storage: Opportunities for fuel storage, batteries, fuel cells, and supercapacitors. *International Journal of Hydrogen Energy*. 2017;42(40):25143–25165. <https://doi.org/10.1016/j.ijhydene.2017.08.103>. doi:10.1016/j.ijhydene.2017.08.103
11. Jia Y, Sun C, Shen S, Zou J, Mao SS, Yao X. Combination of nanosizing and interfacial effect: Future perspective for designing Mg-based nanomaterials for hydrogen storage. *Renewable and Sustainable Energy Reviews*. 2015;44:289–303. <http://dx.doi.org/10.1016/j.rser.2014.12.032>. doi:10.1016/j.rser.2014.12.032
12. Lim KL, Kazemian H, Yaakob Z, Daud WRW. Solid-state materials and methods for hydrogen storage: A critical review. *Chemical Engineering and Technology*. 2010;33(2):213–226. doi:10.1002/ceat.200900376
13. Abbas HF, Wan Daud WMA. Hydrogen production by methane decomposition: A

- review. *International Journal of Hydrogen Energy*. 2010;35(3):1160–1190.
<http://dx.doi.org/10.1016/j.ijhydene.2009.11.036>. doi:10.1016/j.ijhydene.2009.11.036
14. Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. *International Journal of Hydrogen Energy*. 2014;40(34):11094–11111.
<http://dx.doi.org/10.1016/j.ijhydene.2014.12.035>. doi:10.1016/j.ijhydene.2014.12.035
15. Hydrogen Storage. Hydrogen and Fuel Cell Technologies Office. [accessed 2020 Jun 1].
<https://www.energy.gov/eere/fuelcells/hydrogen-storage>
16. Kobayashi H, Hayakawa A, Somarathne KDKA, Okafor EC. Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*. 2019;37(1):109–133.
<https://doi.org/10.1016/j.proci.2018.09.029>. doi:10.1016/j.proci.2018.09.029
17. Ross DK. Hydrogen storage: The major technological barrier to the development of hydrogen fuel cell cars. *Vacuum*. 2006;80(10):1084–1089.
doi:10.1016/j.vacuum.2006.03.030
18. Appl M. Ammonia, 1 Introduction. *Ullmann's Encyclopedia of Industrial Chemistry*. 2012;3:107–137. doi:10.1002/14356007.a02
19. Yin SF, Xu BQ, Zhou XP, Au CT. A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications. *Applied Catalysis A: General*. 2004;277(1–2):1–9. doi:10.1016/j.apcata.2004.09.020
20. Choudhary TV, Sivadinarayana C, Goodman DW. Catalytic ammonia decomposition: CO_x-free hydrogen production for fuel cell applications. *Catalysis Letters*. 2001;72(3–4):197–201.

21. Torrente-Murciano L, Hill AK, Bell TE. Ammonia decomposition over cobalt/carbon catalysts—Effect of carbon support and electron donating promoter on activity. *Catalysis Today*. 2017;286:131–140. <http://dx.doi.org/10.1016/j.cattod.2016.05.041>. doi:10.1016/j.cattod.2016.05.041
22. Li Y, Liu S, Yao L, Ji W, Au CT. Core-shell structured iron nanoparticles for the generation of CO_x-free hydrogen via ammonia decomposition. *Catalysis Communications*. 2010;11(5):368–372. <http://dx.doi.org/10.1016/j.catcom.2009.11.003>. doi:10.1016/j.catcom.2009.11.003
23. Yin SF, Xu BQ, Ng CF, Au CT. Nano Ru/CNTs: A highly active and stable catalyst for the generation of CO_x-free hydrogen in ammonia decomposition. *Applied Catalysis B: Environmental*. 2004;48(4):237–241. doi:10.1016/j.apcatb.2003.10.013
24. Appl M. Ammonia, 2 Production Processes. *Encyclopedia of industrial chemistry*. 2011:139–225. doi:10.1002/14356007.o02
25. Yin SF, Zhang QH, Xu BQ, Zhu WX, Ng CF, Au CT. Investigation on the catalysis of CO_x-free hydrogen generation from ammonia. *Journal of Catalysis*. 2004;224(2):384–396. doi:10.1016/j.jcat.2004.03.008
26. Backes C, Abdelkader AM, Alonso C, Andrieux-Ledier A, Arenal R, Azpeitia J, Balakrishnan N, Banszerus L, Barjon J, Bartali R, et al. Production and processing of graphene and related materials. *2D Materials*. 2020;7(2). doi:10.1088/2053-1583/ab1e0a
27. Singh RK, Kumar R, Singh DP. Graphene oxide: Strategies for synthesis, reduction and frontier applications. *RSC Advances*. 2016;6(69):64993–65011. doi:10.1039/c6ra07626b
28. Brodie VBC. Atomgewicht des Graphils ;

29. Staudenmaier L. Method for the preparation of the graphite acid. *European Journal of Inorganic Chemistry*. 1898;31(2):1481–1487.
30. Hofmann U, König E. Untersuchungen über Graphitoxyd. *Zeitschrift für anorganische und allgemeine Chemie*. 1937;234(4):311–336. doi:10.1002/zaac.19372340405
31. Hummers WS, Offeman RE. Preparation of Graphitic Oxide. *Journal of the American Chemical Society*. 1958;80(6):1339. doi:10.1021/ja01539a017
32. Marcano DC, Kosynkin D V., Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM. Improved synthesis of graphene oxide. *ACS Nano*. 2010;4(8):4806–4814. doi:10.1021/nn1006368
33. Sarac Oztuna FE, Yagci MB, Unal U. First-Row Transition-Metal Cations (Co $^{2+}$, Ni $^{2+}$, Mn $^{2+}$, Fe $^{2+}$) and Graphene (Oxide) Composites: From Structural Properties to Electrochemical Applications. *Chemistry - A European Journal*. 2019;25(12):3131–3140. doi:10.1002/chem.201806309
34. Nicolosi V, Chhowalla M, Kanatzidis MG, Strano MS, Coleman JN. Liquid exfoliation of layered materials. *Science*. 2013;340(6139):72–75. doi:10.1126/science.1226419
35. Yang S, Lohe MR, Müllen K, Feng X. New-Generation Graphene from Electrochemical Approaches: Production and Applications. *Advanced Materials*. 2016;28(29):6213–6221. doi:10.1002/adma.201505326
36. Gao W, Alemany LB, Ci L, Ajayan PM. New insights into the structure and reduction of graphite oxide. *Nature Chemistry*. 2009;1(5):403–408. <http://dx.doi.org/10.1038/nchem.281>. doi:10.1038/nchem.281

37. Park S, An J, Potts JR, Velamakanni A, Murali S, Ruoff RS. Hydrazine-reduction of graphite- and graphene oxide. *Carbon*. 2011;49(9):3019–3023. <http://dx.doi.org/10.1016/j.carbon.2011.02.071>. doi:10.1016/j.carbon.2011.02.071
38. Bo Z, Shuai X, Mao S, Yang H, Qian J, Chen J, Yan J, Cen K. Green preparation of reduced graphene oxide for sensing and energy storage applications. *Scientific Reports*. 2014;4:1–8. doi:10.1038/srep04684
39. Dreyer DR, Murali S, Zhu Y, Rouff RS, Bielawski CW. Reduction of Graphite Oxide Using Alcohols. *Journal of Materials Chemistry*. 2010;(c):1–18.
40. Sheng KX, Xu YX, Li C, Shi GQ. High-performance self-assembled graphene hydrogels prepared by chemical reduction of graphene oxide. *Xinxing Tan Cailiao/New Carbon Materials*. 2011;26(1):9–15. doi:10.1016/S1872-5805(11)60062-0
41. Sarac Oztuna FE, Beyazay T, Unal U. Facile Synthesis of Graphene Aerogel Supported Nickel/Nickel Oxide Core-Shell Nanoparticles: Efficient Electrocatalysts for Oxygen Evolution Reactions. *Journal of Physical Chemistry C*. 2019;123(46):28131–28141. doi:10.1021/acs.jpcc.9b07460
42. Huh SH. Thermal reduction of graphene oxide. *Physics and Applications of Graphene-Experiments*. 2011:73–90.
43. Schneider M, Baiker A. Aerogels in Catalysis. *Catalysis Reviews*. 1995;37(4):515–556. doi:10.1080/01614949508006450
44. Cheng Y, Zhou S, Hu P, Zhao G, Li Y, Zhang X, Han W. Enhanced mechanical, thermal, and electric properties of graphene aerogels via supercritical ethanol drying and high-Temperature thermal reduction. *Scientific Reports*. 2017;7(1):1–11. doi:10.1038/s41598-

45. Alemán J, Chadwick A V., He J, Hess M, Horie K, Jones RG, Kratochvíl P, Meisel I, Mita I, Moad G, et al. Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC recommendations 2007). *Pure and Applied Chemistry*. 2007;79(10):1801–1829. doi:10.1351/pac200779101801
46. Hüsing N, Schubert U. Aerogels—Airy Materials: Chemistry, Structure, and Properties. *Angewandte Chemie International Edition*. 1998;37(1/2):22–45. doi:10.1002/1521-3773(19980202)37:1/2<22::aid-anie22>3.3.co;2-9
47. Mao J, Iocozzia J, Huang J, Meng K, Lai Y, Lin Z. Graphene aerogels for efficient energy storage and conversion. *Energy and Environmental Science*. 2018;11(4):772–799. doi:10.1039/c7ee03031b
48. Chen W, Yan L. In situ self-assembly of mild chemical reduction graphene for three-dimensional architectures. *Nanoscale*. 2011;3(8):3132–3137. doi:10.1039/c1nr10355e
49. Zhang X, Heinonen S, Levänen E. Applications of supercritical carbon dioxide in materials processing and synthesis. *RSC Advances*. 2014;4(105):61137–61152. doi:10.1039/c4ra10662h
50. Han Z, Tang Z, Li P, Yang G, Zheng Q, Yang J. Ammonia solution strengthened three-dimensional macro-porous graphene aerogel. *Nanoscale*. 2013;5(12):5462–5467. doi:10.1039/c3nr00971h
51. Wu X, Zhou J, Xing W, Wang G, Cui H, Zhuo S, Xue Q, Yan Z, Qiao SZ. High-rate capacitive performance of graphene aerogel with a superhigh C/O molar ratio. *Journal of Materials Chemistry*. 2012;22(43):23186–23193. doi:10.1039/c2jm35278h

52. Liu R, Wan L, Liu S, Pan L, Wu D, Zhao D. An interface-induced co-assembly approach towards ordered mesoporous carbon/graphene aerogel for high-performance supercapacitors. *Advanced Functional Materials*. 2015;25(4):526–533. doi:10.1002/adfm.201403280
53. He T, Wang S, Lu F, Zhang M, Zhang X, Xu L. Controllable synthesis of hierarchical NiCo₂S₄@Ni₃S₂ core-shell nanotube arrays with excellent electrochemical performance for aqueous asymmetric supercapacitors. *RSC Advances*. 2016;6(99):97352–97362. doi:10.1039/c6ra21284k
54. Higgins D, Zamani P, Yu A, Chen Z. The application of graphene and its composites in oxygen reduction electrocatalysis: A perspective and review of recent progress. *Energy and Environmental Science*. 2016;9(2):357–390. <http://dx.doi.org/10.1039/C5EE02474A>. doi:10.1039/c5ee02474a
55. Anthonysamy SBI, Afandi SB, Khavarian M, Mohamed AR Bin. A review of carbon-based and non-carbon-based catalyst supports for the selective catalytic reduction of nitric oxide. *Beilstein Journal of Nanotechnology*. 2018;9(1):740–761. doi:10.3762/bjnano.9.68
56. Lu AH, Nitz JJ, Comotti M, Weidenthaler C, Schlichte K, Lehmann CW, Terasaki O, Schüth F. Spatially and size selective synthesis of Fe-based nanoparticles on ordered mesoporous supports as highly active and stable catalysts for ammonia decomposition. *Journal of the American Chemical Society*. 2010;132(40):14152–14162. doi:10.1021/ja105308e
57. Geim AK. Graphene: Status and prospects. *Science*. 2009;324(5934):1530–1534. doi:10.1126/science.1158877
58. Peigney A, Laurent C, Flahaut E, Bacsá RR, Rousset A. Specific surface area of carbon

nanotubes and bundles of carbon nanotubes. *Carbon*. 2001;39(4):507–514.
doi:10.1016/S0008-6223(00)00155-X

59. Choi HJ, Jung SM, Seo JM, Chang DW, Dai L, Baek JB. Graphene for energy conversion and storage in fuel cells and supercapacitors. *Nano Energy*. 2012;1(4):534–551.
<http://dx.doi.org/10.1016/j.nanoen.2012.05.001>. doi:10.1016/j.nanoen.2012.05.001

60. Podila S, Driss H, Zaman SF, Alhamed YA, Alzahrani AA, Daous MA, Petrov LA. Hydrogen generation by ammonia decomposition using Co/MgO-La₂O₃ catalyst: Influence of support calcination atmosphere. *Journal of Molecular Catalysis A: Chemical*. 2016;414:130–139.
<http://dx.doi.org/10.1016/j.molcata.2016.01.012>.
doi:10.1016/j.molcata.2016.01.012

61. Hu ZPP, Chen L, Chen C, Yuan ZYY. Fe/ZSM-5 catalysts for ammonia decomposition to CO_x-free hydrogen: Effect of SiO₂/Al₂O₃ ratio. *Molecular Catalysis*. 2018;455(May):14–22. doi:10.1016/j.mcat.2018.05.027

62. Lara-García HA, Mendoza-Nieto JA, Pfeiffer H, Torrente-Murciano L. CO_x-free hydrogen production from ammonia on novel cobalt catalysts supported on 1D titanate nanotubes. *International Journal of Hydrogen Energy*. 2019;44(57):30062–30074.
doi:10.1016/j.ijhydene.2019.09.120

63. Meng T, Xu QQ, Li YT, Chang JL, Ren TZ, Yuan ZY. Nickle nanoparticles highly dispersed on reduced graphene oxide for ammonia decomposition to hydrogen. *Journal of Industrial and Engineering Chemistry*. 2015;32:373–379.
<http://dx.doi.org/10.1016/j.jiec.2015.09.017>. doi:10.1016/j.jiec.2015.09.017

64. Monshi A, Foroughi MR, Monshi MR. Modified Scherrer Equation to Estimate More

Accurately Nano-Crystallite Size Using XRD. *World Journal of Nano Science and Engineering*. 2012;02(03):154–160. doi:10.4236/wjnse.2012.23020

65. Ganguly A, Sharma S, Papakonstantinou P, Hamilton J. Probing the thermal deoxygenation of graphene oxide using high-resolution in situ X-ray-based spectroscopies. *Journal of Physical Chemistry C*. 2011;115(34):17009–17019. doi:10.1021/jp203741y

66. Matsumoto Y, Koinuma M, Ida S, Hayami S, Taniguchi T, Hatakeyama K, Tateishi H, Watanabe Y, Amano S. Photoreaction of graphene oxide nanosheets in water. *Journal of Physical Chemistry C*. 2011;115(39):19280–19286. doi:10.1021/jp206348s

67. Öztuna FE. Graphene (oxide) – metal/metal (hydr)oxide composites: Synthesis and applications in electrochemical energy storage and conversion. Koç University; 2018.

68. Zickler GA, Smarsly B, Gierlinger N, Peterlik H, Paris O. A reconsideration of the relationship between the crystallite size L_a of carbons determined by X-ray diffraction and Raman spectroscopy. *Carbon*. 2006;44(15):3239–3246. doi:10.1016/j.carbon.2006.06.029

69. López-Díaz D, López Holgado M, García-Fierro JL, Velázquez MM. Evolution of the Raman Spectrum with the Chemical Composition of Graphene Oxide. *Journal of Physical Chemistry C*. 2017;121(37):20489–20497. doi:10.1021/acs.jpcc.7b06236

70. Pimenta MA, Dresselhaus G, Dresselhaus MS, Cançado LG, Jorio A, Saito R. Studying disorder in graphite-based systems by Raman spectroscopy. *Physical Chemistry Chemical Physics*. 2007;9(11):1276–1291. doi:10.1039/b613962k

71. Kaniyoor A, Ramaprabhu S. A Raman spectroscopic investigation of graphite oxide derived graphene. *AIP Advances*. 2012;2(3). doi:10.1063/1.4756995

72. Sitko R, Turek E, Zawisza B, Malicka E, Talik E, Heimann J, Gagor A, Feist B, Wrzalik R. Adsorption of divalent metal ions from aqueous solutions using graphene oxide. *Dalton Transactions*. 2013;42(16):5682–5689. doi:10.1039/c3dt33097d
73. Konkana B, Vasudevan S. Understanding aqueous dispersibility of graphene oxide and reduced graphene oxide through p K a measurements. *Journal of Physical Chemistry Letters*. 2012;3(7):867–872. doi:10.1021/jz300236w
74. Guo H, Wang X, Qian Q, Wang F, Xia X. A Green Approach to the Synthesis of Graphene Nanosheets. *ACS Nano*. 2009;3(9):2653–2659. doi:10.1021/nn900227d
75. Jeong HK, Yun PL, Lahaye RJWE, Park MH, Kay HA, Ick JK, Yang CW, Chong YP, Ruoff RS, Young HL. Evidence of graphitic AB stacking order of graphite oxides. *Journal of the American Chemical Society*. 2008;130(4):1362–1366. doi:10.1021/ja076473o
76. Sui ZY, Meng QH, Li JT, Zhu JH, Cui Y, Han BH. High surface area porous carbons produced by steam activation of graphene aerogels. *Journal of Materials Chemistry A*. 2014;2(25):9891–9898. doi:10.1039/c4ta01387e
77. Díez-Betriu X, Álvarez-García S, Botas C, Álvarez P, Sánchez-Marcos J, Prieto C, Menéndez R, De Andrés A. Raman spectroscopy for the study of reduction mechanisms and optimization of conductivity in graphene oxide thin films. *Journal of Materials Chemistry C*. 2013;1(41):6905–6912. doi:10.1039/c3tc31124d
78. Ni ZH, Wang HM, Ma Y, Kasim J, Wu YH, Shen ZX. Tunable Stress and Controlled Thickness Modification in Graphene by Annealing. 2008;2(5):1033–1039.
79. Sarac Oztuna FE, Barim SB, Bozbag SE, Yu H, Aindow M, Unal U, Erkey C. Graphene Aerogel Supported Pt Electrocatalysts for Oxygen Reduction Reaction by Supercritical

Deposition. Electrochimica Acta. 2017;250:174–184.

<http://dx.doi.org/10.1016/j.electacta.2017.08.067>. doi:10.1016/j.electacta.2017.08.067

80. Tang H, Ehlert GJ, Lin Y, Sodano HA. Highly efficient synthesis of graphene nanocomposites. *Nano Letters*. 2012;12(1):84–90. doi:10.1021/nl203023k

81. Liu Z, Ciais P, Deng Z, Lei R, Davis SJ, Feng S, Zheng B, Cui D, Dou X, He P, et al. Near-real-time data captured record decline in global CO₂ emissions due to COVID-19. *arXiv*. 2020:1–45. doi:2004.13614v3

82. Le Quéré C, Jackson RB, Jones MW, Smith AJP, Abernethy S, Andrew RM, De-Gol AJ, Willis DR, Shan Y, Canadell JG, et al. Temporary reduction in daily global CO₂ emissions during the COVID-19 forced confinement. *Nature Climate Change*. 2020;10(7):647–653. <http://dx.doi.org/10.1038/s41558-020-0797-x>. doi:10.1038/s41558-020-0797-x

83. Yin SF, Zhang QH, Xu BQ, Zhu WX, Ng CF, Au CT. Investigation on the catalysis of CO_x-free hydrogen generation from ammonia. *Journal of Catalysis*. 2004;224(2):384–396. doi:10.1016/j.jcat.2004.03.008

84. Jakubek T, Kaspera W, Legutko P, Stelmachowski P, Kotarba A. How to Efficiently Promote Transition Metal Oxides by Alkali Towards Catalytic Soot Oxidation. *Topics in Catalysis*. 2016;59(10–12):1083–1089. doi:10.1007/s11244-016-0595-x

85. Liu R, Xu Y, Li Z, Ma X. A Facile and Efficient Modification of CNTs for Improved Fischer-Tropsch Performance on Iron Catalyst: Alkali Modification. *ChemCatChem*. 2016;8(8):1454–1458. doi:10.1002/cctc.201501219

86. Bakar FIA, Ismail S, Nurulnabilah A, Shahadan MS. Synthesis of α -Fe₂O₃ Nanowires/MWCNTS Composite for Photocatalyst. *Journal of Physics: Conference Series*.

2018;1082(1). doi:10.1088/1742-6596/1082/1/012048

87. Doong RA, Saha S, Lee CH, Lin HP. Mesoporous silica supported bimetallic Pd/Fe for enhanced dechlorination of tetrachloroethylene. *RSC Advances*. 2015;5(110):90797–90805. <http://dx.doi.org/10.1039/C5RA15070A>. doi:10.1039/c5ra15070a

88. Sanetuntikul J, Chuaicham C, Choi YW, Shanmugam S. Investigation of hollow nitrogen-doped carbon spheres as non-precious Fe-N₄ based oxygen reduction catalysts. *Journal of Materials Chemistry A*. 2015;3(30):15473–15481. doi:10.1039/c5ta02677f

89. Graat PCJ, Somers MAJ. Simultaneous determination of composition and thickness of thin iron-oxide films from XPS Fe 2p spectra. *Applied Surface Science*. 1996;100–101:36–40. doi:10.1016/0169-4332(96)00252-8

90. Biesinger MC, Payne BP, Grosvenor AP, Lau LWM, Gerson AR, Smart RSC. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Applied Surface Science*. 2011;257(7):2717–2730. <http://dx.doi.org/10.1016/j.apsusc.2010.10.051>. doi:10.1016/j.apsusc.2010.10.051

91. Zier M, Scheiba F, Oswald S, Thomas J, Goers D, Scherer T, Klose M, Ehrenberg H, Eckert J. Lithium dendrite and solid electrolyte interphase investigation using OsO₄. *Journal of Power Sources*. 2014;266:198–207. <http://dx.doi.org/10.1016/j.jpowsour.2014.04.134>. doi:10.1016/j.jpowsour.2014.04.134

92. Goodwin Jr. JG, Kim S, Rhodes WD. Turnover frequencies in metal catalysis: Meanings, functionalities and relationships. 2007;17:320–348. doi:10.1039/9781847553294-00320

93. Grosman M, Löffler DG. Kinetics of ammonia decomposition on polycrystalline tungsten. *Journal of Catalysis*. 1983;80(1):188–193. doi:10.1016/0021-9517(83)90242-7

94. Laidler KJ. The development of the arrhenius equation. *Journal of Chemical Education*. 1984;61(6):494–498. doi:10.1021/ed061p494
95. Ghampson IT, Newman C, Kong L, Pier E, Hurley KD, Pollock RA, Walsh BR, Goundie B, Wright J, Wheeler MC, et al. Effects of pore diameter on particle size, phase, and turnover frequency in mesoporous silica supported cobalt Fischer-Tropsch catalysts. *Applied Catalysis A: General*. 2010;388(1–2):57–67. <http://dx.doi.org/10.1016/j.apcata.2010.08.028>. doi:10.1016/j.apcata.2010.08.028
96. Finger LW, Hazen RM. Crystal structure and isothermal compression of Fe_2O_3 , Cr_2O_3 , and V_2O_3 to 50 kbars. *Journal of Applied Physics*. 1980;51(10):5362–5367. doi:10.1063/1.327451
97. Jack KH. The iron–nitrogen system: the crystal structures of ϵ -phase iron nitrides. *Acta Crystallographica*. 1952;5(4):404–411. doi:10.1107/s0365110x52001258
98. Duan X, Qian G, Zhou X, Sui Z, Chen D, Yuan W. Tuning the size and shape of Fe nanoparticles on carbon nanofibers for catalytic ammonia decomposition. *Applied Catalysis B: Environmental*. 2011;101(3–4):189–196. <http://dx.doi.org/10.1016/j.apcatb.2010.09.017>. doi:10.1016/j.apcatb.2010.09.017
99. Cui HZ, Gu YQ, He XX, Wei S, Jin Z, Jia CJ, Song QS. Iron-based composite nanostructure catalysts used to produce CO_x -free hydrogen from ammonia. *Science Bulletin*. 2016;61(3):220–226. doi:10.1007/s11434-015-0991-9
100. Hu ZP, Chen L, Chen C, Yuan ZY. Fe/ZSM-5 catalysts for ammonia decomposition to CO_x -free hydrogen: Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. *Molecular Catalysis*. 2018;455(February):14–22. doi:10.1016/j.mcat.2018.05.027

101. Zhang J, Comotti M, Schüth F, Schlögl R, Su DS. Commercial Fe- or Co-containing carbon nanotubes as catalysts for NH_3 decomposition. *Chemical Communications*. 2007;(19):1916–1918. doi:10.1039/b700969k
102. Zhang H, Gong Q, Ren S, Arshid MA, Chu W, Chen C. Implication of iron nitride species to enhance the catalytic activity and stability of carbon nanotubes supported Fe catalysts for carbon-free hydrogen production via low-temperature ammonia decomposition. *Catalysis Science and Technology*. 2018;8(3):907–915. doi:10.1039/c7cy02270k
103. Ohtsuka Y, Xu C, Kong D, Tsubouchi N. Decomposition of ammonia with iron and calcium catalysts supported on coal chars. *Fuel*. 2004;83(6):685–692. doi:10.1016/j.fuel.2003.05.002
104. Lorenzuti B, Montini T, Bevilacqua M, Fornasiero P. FeMo-based catalysts for H_2 production by NH_3 decomposition. *Applied Catalysis B: Environmental*. 2012;125:409–417. doi:10.1016/j.apcatb.2012.06.011
105. Kurtoğlu SF, Soyer-Uzun S, Uzun A. Modifying the structure of red mud by simple treatments for high and stable performance in CO_x -free hydrogen production from ammonia. *International Journal of Hydrogen Energy*. 2018;43(45):20525–20537. doi:10.1016/j.ijhydene.2018.09.032
106. Love KS, Brunauer S. The Effect of Alkali Promoter Concentration on the Decomposition of Ammonia Over Doubly Promoted Iron Catalysts*. *Journal of the American Chemical Society*. 1942;64(4):745–751.
107. Choi HC, Shim M, Bangsaruntip S, Dai H. Spontaneous reduction of metal ions on the sidewalls of carbon nanotubes. *Journal of the American Chemical Society*.

2002;124(31):9058–9059. doi:10.1021/ja026824t

108. Howard CA, Dean MPM, Withers F. Phonons in potassium-doped graphene: The effects of electron-phonon interactions, dimensionality, and adatom ordering. *Physical Review B - Condensed Matter and Materials Physics*. 2011;84(24):1–4. doi:10.1103/PhysRevB.84.241404

109. Wei W, Wang G, Yang S, Feng X, Müllen K. Efficient coupling of nanoparticles to electrochemically exfoliated graphene. *Journal of the American Chemical Society*. 2015;137(16):5576–5581. doi:10.1021/jacs.5b02284

110. Yu X, Wei Y, Liu C, Ma J, Liu H, Wei S, Deng W, Xiang J, Luo S. Ultrafast and deep removal of arsenic in high-concentration wastewater: A superior bulk adsorbent of porous Fe₂O₃ nanocubes-impregnated graphene aerogel. *Chemosphere*. 2019;222:258–266. <https://doi.org/10.1016/j.chemosphere.2019.01.130>. doi:10.1016/j.chemosphere.2019.01.130

111. Hu ZP, Chen L, Chen C, Yuan ZY. Fe/ZSM-5 catalysts for ammonia decomposition to CO_x-free hydrogen: Effect of SiO₂/Al₂O₃ ratio. *Molecular Catalysis*. 2018;455(February):14–22. doi:10.1016/j.mcat.2018.05.027

112. Xue XY, Yuan S, Xing LL, Chen ZH, He B, Chen YJ. Porous Co₃O₄ nanoneedle arrays growing directly on copper foils and their ultrafast charging/discharging as lithium-ion battery anodes. *Chemical Communications*. 2011;47(16):4718–4720. doi:10.1039/c1cc10462d

113. Xu Q, Chandra M. Catalytic activities of non-noble metals for hydrogen generation from aqueous ammonia-borane at room temperature. *Journal of Power Sources*. 2006;163(1 SPEC.

ISS.):364–370. doi:10.1016/j.jpowsour.2006.09.043

114. Cao L, Ma L, Xiao P, Zhang Y, Zhang S, Yang S. Vertically aligned cobalt oxide nanowires on graphene networks for high-performance lithium storage. *Nanotechnology*. 2014;25(44). doi:10.1088/0957-4484/25/44/445704

115. Zhang H, Alhamed YA, Kojima Y, Al-zahrani AA, Petrov LA. Cobalt Supported on Carbon Nanotubes. An Efficient Catalyst for Ammonia Decomposition. *Comptes Rendus de l'Academie Bulgare des Sciences*. 2013;44(48):519–524.

116. Wang Y, Kunz M, Siebers S, Rollins H, Gleaves J, Yablonsky G, Fushimi R. Transient Kinetic Experiments within the High Conversion Domain: The Case of Ammonia Decomposition. *Catalysts*. 2019;9(1):104. doi:10.3390/catal9010104

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