

**CARBON DIOXIDE HYDROGENATION ON
ALUMINA SUPPORTED RUTHENIUM
CATALYSTS**

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ABSTRACT

CARBON DIOXIDE HYDROGENATION ON ALUMINA SUPPORTED RUTHENIUM CATALYSTS

In this study, the effect of basicity of catalyst is investigated using different metal oxides supported Nickel and Ruthenium catalysts. The basic strength of catalysts was manipulated by using different types of metals and different composition of supports. In this study $\text{Al}_2\text{O}_3\text{-CaO}$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-BaO}$ supports were used to make supported nickel or ruthenium catalyst, which synthesized with a sol-gel method. Different mass ratios of supports were used such as; 100%, 70%/30%, 50%/50%, 20%/80% for all the mixed oxides. For all the metal oxides, nickel loadings are 1 %, 5% and Ruthenium loading is 0.5%. Calcination temperature was 500 °C and calcination time was 6 hours. All the catalysts were used in methanation reaction with conditions varies between 300-600 °C, inlet ratio of $\text{CO}_2/\text{H}_2 \sim 1:5$ and GSHV 5000h^{-1} . The gas products were analyzed using GC and the catalysts were characterized using XRD, $\text{NH}_3\text{-TPD}$ and BET.

Nickel load selected as 1%, magnesium supported catalysts' the main crystallites were aluminum oxide and magnesium oxide for 30%,50%,80; respectively. Calcium supported catalyst had had alumina and calcium oxide crystallites for 30% and 50%, respectively. Barium supported catalysts had had alumina and barium mix oxide crystallites for 30% and 50% loadings, respectively. For 5% Nickel loaded 70-30% alumina magnesia mix oxide catalyst, magnesia and alumina crystallites were found.

Aluminum magnesium mix oxide catalysts had higher basicity than aluminum barium mix oxide catalysts for 1% nickel catalysts. Ruthenium based magnesium alumina mix oxide catalyst had higher basicity than nickel-based magnesium alumina catalysts. Ruthenium catalysts had higher total performance towards both of the reverse water gas shift reaction and carbon dioxide methanation than nickel-based catalysts

ÖZET

ALUMİNYUM OKSİT DESTEKLİ RUTİNYUM METAL KATALİZÖRLER ÜZERİNDE KARBONDİOKSİT HİDROJENLEMESİ

Bu çalışmada katalizörün bazisitesinin etkisi farklı metal oksit destekli nikel ve rutenyum bazlı katalizörler kullanılarak incelenmiştir. Katalizörlerin bazisitesi farklı oranlarda farklı metal oksitler kullanılarak incelendi. Bu çalışmada Al_2O_3 -CaO, Al_2O_3 -MgO, Al_2O_3 -BaO ile desteklenmiş, nikel ve rutenyum bazlı katalizörler kullanılmıştır. Katalizörlerin sentezinde sol-jel yöntemi kullanılmıştır. Destekler için 70/30,50/50 ve 20/80 oranları seçilmiştir. Metal yüklemeleri nikel için %1 ve %0,5 rutenyum içinse %0,5 olarak seçilmiştir

Tüm katalizörler için kalsinasyon sıcaklığı 500 °C kalsinasyon süresi 6 saat seçilmiştir. Tüm katalizörler için reaksiyon sıcaklığı 300 ile 500 °C arasında seçilmiştir. Katalizörlerin kristal fazı karakterizasyonu XRD ile yapılmıştır. Katalizörlerin bazisitesi CO_2 -TPD ile yapılmıştır. Reaksiyondan çıkan ürünlerin karakterizasyonu gaz kromatografi ile yapılmıştır.

Nikel oranı %1 olarak seçilmiş ve %80 magnezyum olan katalizörlerde alümin kristal fazı, %50 olanlarda magnezyum oksit ve alümin kristal fazı, %80 olanlarda ise magnezyum oksit kristal fazı bulunmuştur. Kalsiyum içinse %30 olanlarda alümin kristal fazı, %50 olanlarda kristal fazı bulunmamıştır. Baryum destekli katalizörde ise, %30 da alümin kristal fazı, 50% baryum oksit kristal fazı bulunmuştur. Nikel oranı %5 olan %70 -30 magnezyum oksit katalizörde ise magnezyum oksit ve alümin kristalleri bulunmuştur.

Nikel bulunduran katalizörler içerisinde alümin ve magnezyum oksit destekli katalizörler alümin ve baryum oksit destekli katalizörlerden daha yüksek bazisiteye sahiptir. Rutenyum bazlı magnezyum oksit ve alümin destekli katalizör ise nikel bulunduran katalizör ise nikel bulunduran magnezyum oksit ve alümin destekli katalizörlerden daha yüksek bazisiteye sahiptir. Rutenyum bazlı katalizörler nikel bazlı katalizörlere göre daha yüksek toplam performansa sahiptir.

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CHAPTER 1

INTRODUCTION

The population of the world was estimated as 7.56 billion in 2017. In 2040 world population was projected as 9 billion in 2040 (International Energy Agency 2017). The growth in population of the world cause more energy demand due to more energy consumption to satisfies expected live quality of world population, the energy demand caused by agricultural activities or industrial needs are also increased (Zabel 2009). Global energy demand increases 28 % between 2015 to 2040 according to International Energy Outlook (U.S Energy Information Agency 2017).

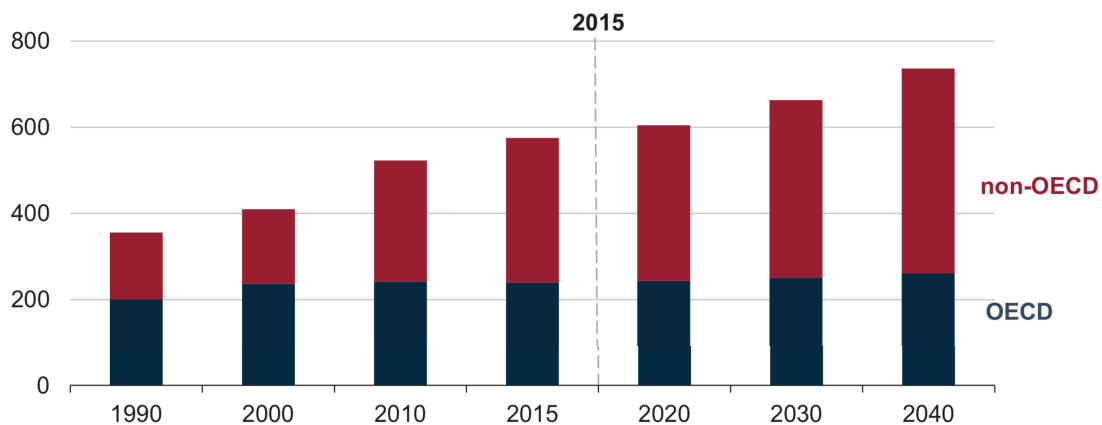


Figure 1: Global Energy Demand between 1990 and 2040 (Source: U.S Energy Information Energy)

Between 2010 to 2016 and 2017 to 2040 investment in energy generation will increase. Investment in renewable sources will increase the most to overcome the environment problems and avoid global warming according to World Energy Outlook 2017(International Energy Agency 2017).

In 2014 40% of electricity generated from coal, 4 % generated from renewable sources such as wind turbine or solar panel. In 2040, electricity generated from coal diminishes to 30 % and renewable sources increases to 10 % with natural gas, and nuclear energy. Between 2014 and 2040 the world shifts to cleaner fuels and more effective process.

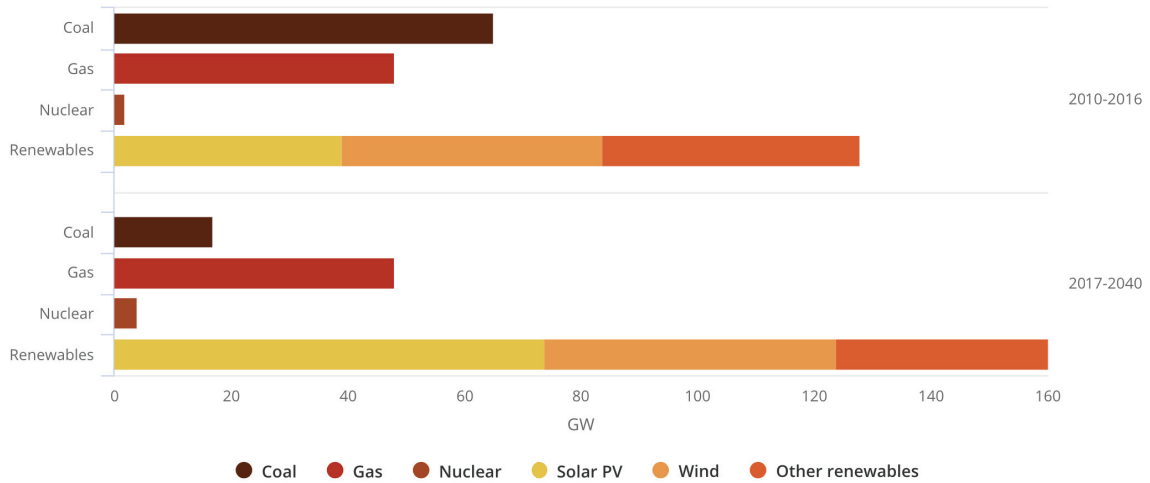


Figure 2: Global Average Annual Net Capacity additions by type (Source: International Energy Agency)

This shift can be caused by more restricted CO₂ emission policies and air quality policies(ExonMobil 2018).

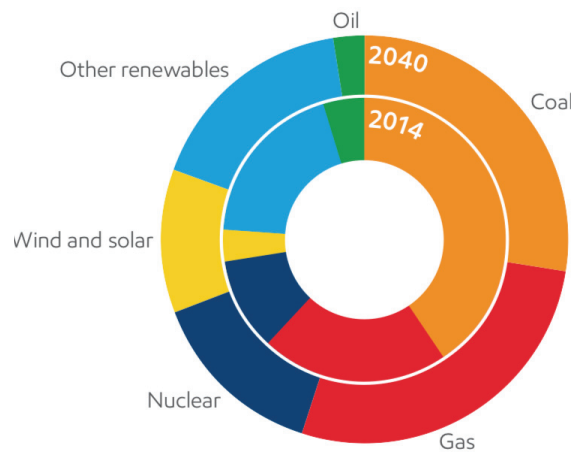


Figure 3: Share of Global Electricity Generation 2014 and 2040 (Source: ExxonMobil)

With advancing technology, the cost for solar PV and Wind turbines become less costly. The cost of coal, natural gas and petroleum became higher because the cost of the new sources for these fossil fuels increased and this cause cost of the energy generated from these sources. To achieve economic stability the new renewable technologies will be used in future with more sophisticated technologies to find new sources for fossil fuels and new energy generation processes from these

fossil fuels. The projections shows that energy generated from all of the sources but the high cost and more environmental polluted sources such as coal, petroleum and natural gas will become less respectively(Solubility Sustainable Intelligence 2014).

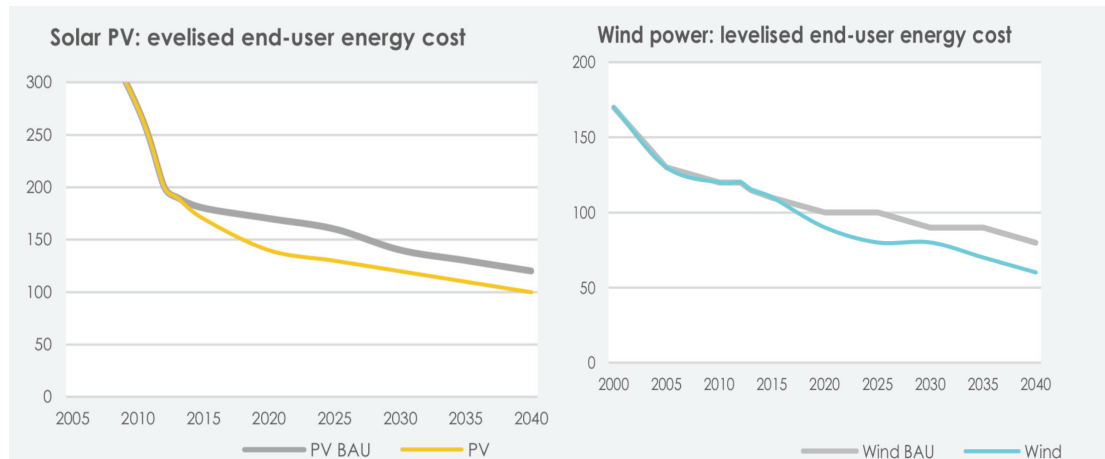


Figure 4: Solar PV and Wind power energy source cost with business as usual and potential (Source: Solubility Sustainable Intelligence)

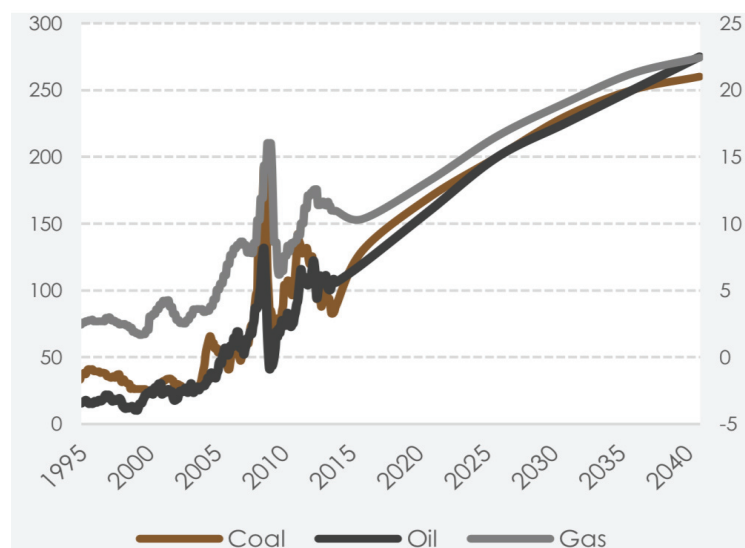


Figure 5: Coal, Oil and Gas prices between 1995 and 2040 (Source: Solubility Sustainable Intelligence)

Environmental issues of sources can affect the usage of sources in the energy generation. To decrease environmental problems and global warming, the new renewable or sustainable energy sources or technologies must be found. With the help of advancing technology and efficiency of the energy consumption, CO₂ emissions generated per unit energy consumed by end users continue to decrease. Under BAU scenario, (Business As Usual), the decrease in CO₂ emission is not enough to avoid

passing the barrier of the irreversible climate change. Also increase in the efficiency of energy generation process does not completely cut off CO₂ emission caused by population and economic growth. If business goes as usual (under BAU scenario), the CO₂ emission caused by energy generation in 2020 will increase 10 % more than the levels of 2013. Most of the CO₂ emission caused by energy generation from fossil fuels such as coal, petroleum, natural gas. Coal causes the most of the CO₂ emission because of the highest carbon content. Under Marshall scenario, CO₂ emission starts to decrease rapidly after 2015 because of the emerging of new technologies that cause much less CO₂ emission per unit of energy generation. Annual CO₂ emission in 2020's will be equal to 2000 and in 2025's CO₂ emission will be equal to 1990's. Because of the low CO₂ emission, caused by energy generation from renewable sources (only the production of tools to generate power from renewable sources or infrastructure of the energy generation), world will use more renewable sources and biggest sources of the carbon dioxide emission will become fossil fuels (Solubility Sustainable Intelligence 2014).

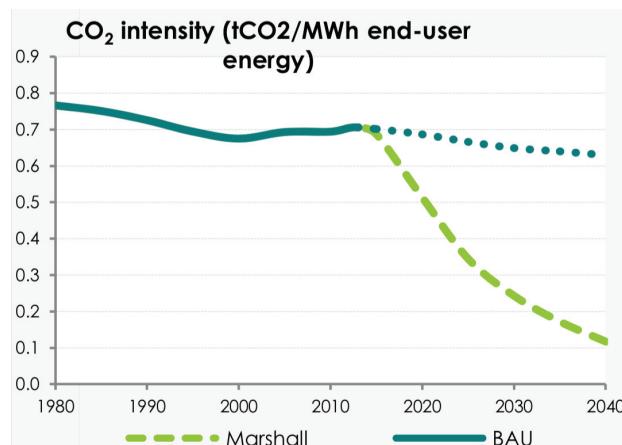


Figure 6: CO₂ intensity of energy consumption under BAU and Marshall scenario, 1980-2040 (Source: Solubility Sustainable Intelligence)

The Marshall scenario does not fit perfectly with actual data; however, it seems that the future can be close to this scenario. The biggest part of the GHG (greenhouse gases) is carbon dioxide. However, there are other GHG that are more hazardous to environment than CO₂. Methane, Nitrous oxides and F- gases are more hazardous to the environment than carbon dioxide. According to Intergovernmental Panel on Climate change, 76% of GHG are carbon dioxide, 16 % are Methane, 6% are Nitrous oxides and 2% are F-gases (IPCC 2014). To overcome hazardous effect of GHG gases, new green technologies must be found.

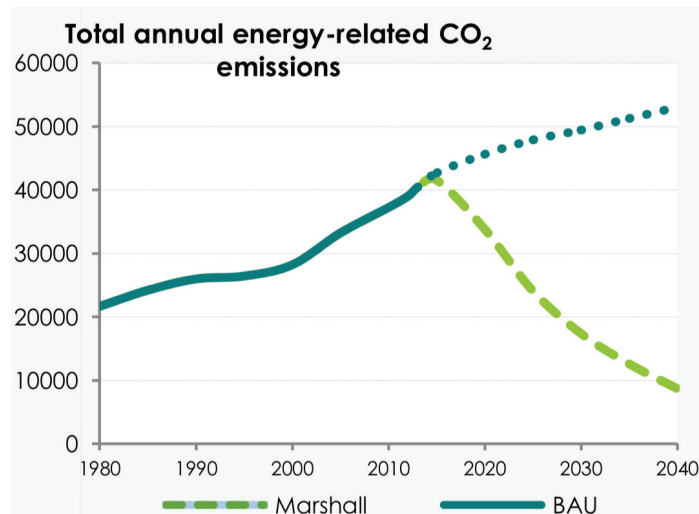


Figure 7: Total annual energy-CO₂ intensity emissions under BAU and Marshall scenario, 1980-2040 (Source: Solubility Sustainable Intelligence)

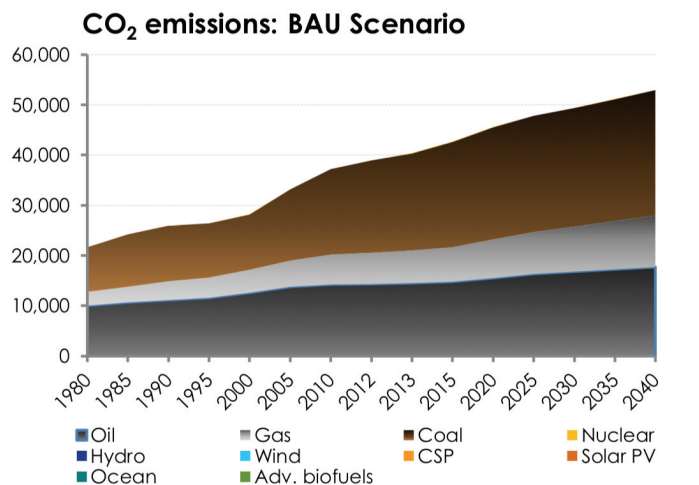


Figure 8: Annual energy-CO₂ emissions by source under BAU scenario, 1980-2040 (Source: Solubility Sustainable Intelligence)

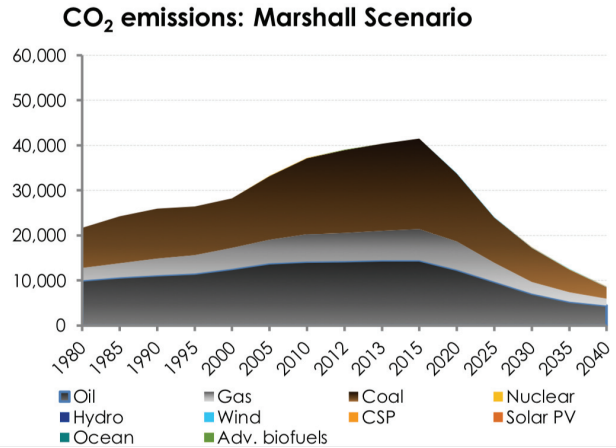


Figure 9: Annual energy-CO₂ emissions by source under Marshall scenario, 1980-2040 (Source: Solubility Sustainable Intelligence)

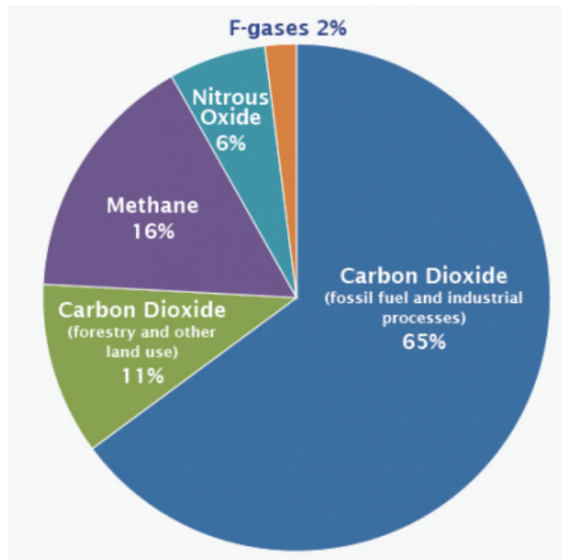


Figure 10: Global Gas Emission by Gas in 2010 (Source IPCC 2014)

Hybrid technologies can be used to achieve sustainable and environment friendly energy generation. There are some presented hybrid technologies, such as one given below.

With this technology; renewable electricity can be effectively stored in large amounts in a chemical fuel (such as H₂ or a syngas, i.e. a mixture of CO and H₂). With low temperature-electrolysis (e.g., PEM and alkaline electrolyzers), H₂ and O₂ are the only products and hydrogen can be employed in fuel cell-vehicles or alternatively stored in the natural gas distribution infrastructure to some extent. Also, hydrogen and carbon dioxide available as byproducts in chemical industries can be

used in carbon dioxide methanation process to produce methane. This methane can be used as natural gas in already exist natural gas systems (Giglio 2015).

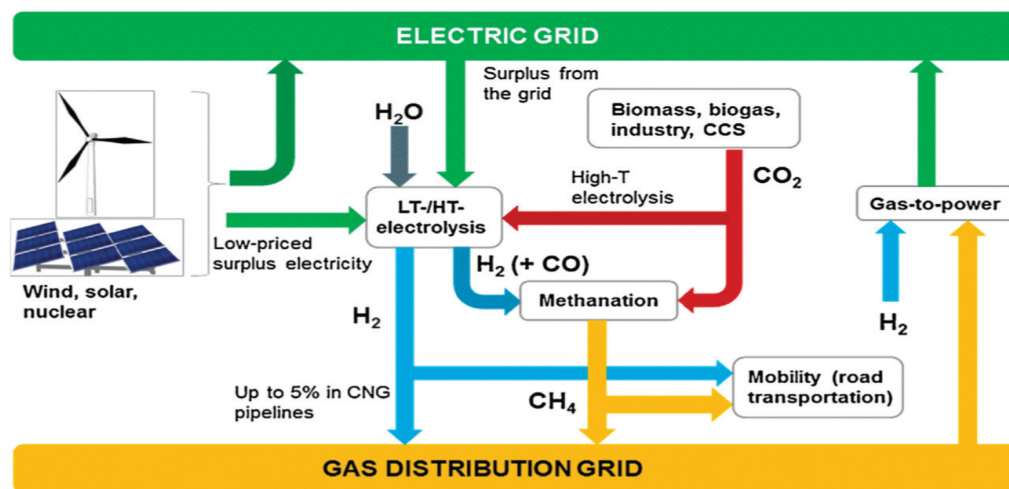


Figure 11: New Hybrid Proposed Technology (Source: Giglio 2015)

In this study, the effect of basicity of catalyst on carbon dioxide methanation was investigated using different metal oxide supported nickel and ruthenium catalysts. The basic strength and basicity of the catalysts was manipulated using different types of metal oxides and their different compositions. In this study, Al₂O₃-CaO, Al₂O₃-MgO, Al₂O₃-BaO mixed support oxides were used with nickel and ruthenium catalyst, which synthesized with a sol-gel method. Different ratios of oxides, such as such as; 100%, 70%/30%, %50/50%, 20%/80%, were used . For all the mixed metal oxides, nickel loading is 1%, 5% and ruthenium loading is 0.5%. Calcination temperature was 500 °C and the calcination time was 6 h. All the catalysts were used in methanation reaction under the conditions of 300-500 °C, inlet ratio of CO₂/H₂ ~1/5 and GSHV 5000h⁻¹. The gas products were analyzed using a GC and catalysts were characterized using XRD, NH₃-TPD and BET.

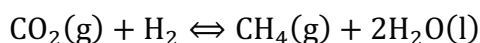
This thesis consists of 5 chapters. First chapter gives general background knowledge on the selected subject as energy demand of the world, new technologies and environmental problem of the world common energy technologies. In Chapter 2, literature review is presented about methanation of carbon dioxide with selected catalysts with different reaction conditions. Third chapter is about material and methods used in this thesis. In Chapter 4, results are presented and discussed the correlation between physicochemical properties of the catalysts and catalyst activities. The final chapter gives the conclusion reached in this study.

CHAPTER 2

LITERATURE SURVEY

2.1 CO₂ Methanation

CO₂ methanation is a process that convert CO₂ to methane. It is also called as CO₂ hydrogenation because of the reaction between CO₂ and hydrogen atom. It is observed first time by Paul Sabatier and Senderens in 1897 at elevated temperature between 300 to 400 °C with nickel catalyst.



The CO₂ hydrogenation is highly exothermic reaction thermodynamically favorable at relatively low temperature such as 250 to 400 °C. Release energy of this reaction is $\Delta H = -165 \text{ kJ/mol}$. The reduction of carbon atom to methane is limited so a catalyst must be used for reaction. This catalyst can be differ between nickel, ruthenium, platinum or alumina(Sabatier and Jean-Baptiste Senderes 1902).

2.2 Catalyst Selection

D- electron transition metals can be used successfully for catalytic purpose. Also, it is known that d electron orbitals cause bond within metal at the surface. Nickel, platinum or ruthenium can break the hydrogen bond in hydrogen and also nickel can break the bond between carbon and oxygen in CO₂. The support material generally selected because having base site because CO₂ is acidic material and adsorb to the catalyst(Richardson 1992). The most investigated catalysts are nickel alumina catalyst. For this study nickel and ruthenium base catalysts with different supports are selected.

IIIB	IVB	VB	VIB	VII B	VIII	IB		
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
La	Hf	Ta	W	Re	Os	Ir	Pt	Au

Figure 12 : Transition d- metals (Source Principles of Catalyst Development Richardson 1989)

2.2.1 Nickel based catalyst

Nickel based catalysts are widely investigated. Supports, preparation method and active metal loads are most important parameters for activity of catalysts. The calcination temperature is also a main effect. Also, important parameter for catalyst is to achieve high selectivity to preferred product. The main problem for nickel-based catalyst is the poisoning or sintering. Nickel like many noble metals can break hydrogen bond in water. Also, nickel can break carbon oxygen bond in carbon dioxide. This carbon will accumulate on the surface of nickel sites of the catalyst and effect negatively activity of catalyst. To overcome this problem, there are lots of different research are made. The most widely investigated support is alumina supported nickel catalysts. Alumina supported nickel catalyst show high activity for reaction however also have carbon poisoning problem with instability at higher temperatures(Takano et al. 2016).

Nickel alumina catalyst with different nickel loadings varies between 5% to 20 % are investigated. These catalysts prepared with impregnation method and with different calcination temperatures. This research investigated effect of calcination temperature and nickel loading on CO₂ conversion and CH₄ selectivity. When nickel loading is 20 % the catalyst is most stable and have highest conversion and selectivity between 200 to 350 °C(Rahmani et al. 2014).

Different researches are made for Nickel alumina catalysts. 10 % Nickel loading alumina catalyst is investigated. Catalyst is prepared with impregnation method. At 516 °C with 11:1 H₂: CO₂ inlet ratio CO₂ conversion and CH₄ selectivity found as 98 % and 100 %. Higher inlet ratio for reaction caused higher selectivity and conversion(Shashidhara and Ravindram 1998).

Silica supported nickel catalysts also are researched widely. Most recently mesostructured silica nanoparticles are found good supports for catalysts. With different types of silica such as mesostructured silica nanoparticles (MCN). Catalysts are prepared with Sol-Gel method. These catalysts are used in reaction between 150 to 450 °C. Activity of these catalysts are found as; highest for MCN silica supported nickel then silica oxide supported nickel and lowest one is alumina supported nickel. Silica oxide supported nickel catalyst also investigated. This catalyst prepared with reverse microemulsion method. This catalyst used at 450 °C with 4:1 H₂: CO₂ inlet

ratio. CO₂ conversion is found as 36.8 and CH₄ selectivity is found as 81.8%(Park and McFarland 2009).

Ceria oxide, titanium oxide or magnesium oxide supported nickel catalyst also an option. 10% nickel ceria catalyst prepared with impregnation method. Effect of the different support is investigated. The reaction occurs at 350 °C with inlet ratio of 4:1 H₂: CO₂. CH₄ selectivity is found as 100% and CO₂ conversion is found as 90%. 10% nickel titanium oxide supported catalysts and 10% nickel magnesium catalysts are prepared with impregnation method. These catalysts are used at 450 °C and inlet ratio of 4:1 H₂: CO₂. For titanium oxide supported and magnesium oxide supported catalysts CO₂ conversion are found as 76% and 70 %, CH₄ selectivity are found as 98% and 97% relatively(Tada et al. 2012).

Nickel with different supports such as magnesia alumina zirconium oxide are investigated. These catalysts promoted with different substances such as silica. This research shows that, there is relationship between pore structure and catalytic activity and lifetime of catalyst. The most active catalyst found as nickel catalyst promoted with silica because of the wide pores that gives highest methane conversion(Ermakova et al. 2000).

Different metal oxide with mixed oxide supported nickel catalysts are investigated. For this research, effect of nickel content is investigated. Metal loads are selected as 5, 10, 15 and 20 % of nickel. zirconium oxide, silica oxide and magnesium aluminum mix oxide are selected as supports. For these catalyst reaction conditions were 350 to 500 °C and constant inlet conditions of CO₂: H₂. Higher temperature is caused higher CO₂ conversion for all catalyst but at 500 °C CO₂ conversion drops because of the carbon sintering for Ni/ZrO₂ catalyst. Ni/ZrO₂ catalyst has the highest catalyst(Martínez et al. 2019).

There are different mixed oxide catalysts. A new research that use quaternary support system that use zirconium oxide, titanium oxide, cerium oxide and alumina. This catalyst is prepared with wet impregnation method at alumina powder as host with different amount of zirconium, titanium and cerium oxide. These three components are equal percentage. For 10 % titanium oxide, 10% cerium oxide and 10% zirconium oxide and 70 % alumina the catalyst named as Ni/C10. The best catalyst is Ni/C15 for CO₂ conversion and selectivity. A higher compositions of metal oxide causes large sized nickel particles. Larger size particles cause higher CO₂

conversion at lower temperatures. At 300 °C CO₂ conversion found as higher than 80%(Abate et al. 2016).

2.2.2 Ruthenium based catalyst

Ruthenium is more active and more stable than nickel. Also, ruthenium does not have carbon poisoning effect because of unable to break carbon oxygen on in CO₂. Ruthenium is much more stable between higher range of operation temperature. However ruthenium is much more expensive than nickel and because of that industrial application of this catalyst are limited(L Kustov A et al. 2007).

Ruthenium catalysts are also widely researched with different support metal oxides and mixed metal oxides. Alumina, titanium oxide, magnesium oxide, silica oxide and aluminum and magnesium mixed oxide are used for supports. The activity in investigated with two different aspect CO₂ conversion and CH₄ yield. These catalysts are used with different temperature range of 250 to 500 °C. Highest activity found with 3% ruthenium with alumina support. At 400 °C methane conversion found as nearly 80% and CO₂ conversion found as higher than 80%(Garbarino et al. 2015).

There are different studies using titanium oxide with different ruthenium amount. Ruthenium amount varies between 0.75 to 0.8 %. Three different catalyst prepared with different ruthenium amount and different preparation method. 0.8 % ruthenium with titanium oxide support that prepared with sputter deposition method. This catalyst used in reaction with condition at 160 °C and 4:1 H₂: CO₂ inlet condition achieved 100% methane yield. 0.76 % ruthenium with titanium oxide support that prepared with gratzel method. This catalyst used in reaction with condition at 250 °C and 4:1 H₂: CO₂ inlet condition achieved 100% methane yield. 0.75 % ruthenium with titanium oxide support that prepared with incipient wet impregnation method. This catalyst used in reaction with condition at 385 °C and 4:1 H₂: CO₂ inlet condition achieved 100% methane yield(Abe et al. 2009).

Microlith is sued as support for ruthenium catalyst. This study used different temperature and different inlet ratio to understand the effect. 4:1 and 5.5:1 H₂: CO₂ inlet ratio is used. For ruthenium microlith catalyst 4:1 inlet ratio at 360 °C temperature is used and achieved 83.5% CO₂ conversion and 100% methane selectivity. Also 4:1 inlet ratio at 395 °C temperature is used and achieved 92% CO₂ conversion and 100% methane selectivity. For 5.5:1 H₂: CO₂ inlet condition at 225 °C temperature is used and achieved 99.8% CO₂ conversion and 100% methane

selectivity and for 350⁰C temperature 93 % CO₂ conversion and 100% methane selectivity is achieved(Junaedi et al. 2012).

Ruthenium based catalyst are investigated with different supports such as zeolites. The effect of metal loading is investigated for this study. Increase in metal loading cause higher ruthenium particle size. Increase in particles size also cause higher activity for CO₂ methanation. Selectivity for methane does not change(Eckle et al. 2012).

Ceria oxide also can be used as ruthenium catalyst. In this study, different amount of ruthenium metal as active site in catalyst. Ruthenium amount is varying between 1 % to 5 %. These catalysts prepared with combustion method. These catalysts are used in same inlet ratio 4:1 H₂: CO₂ and with different temperature between 500 to 450 ⁰C. The best results for each catalyst determined at 500 ⁰C, 500 ⁰C, 500 ⁰C, 480 ⁰C, 450 ⁰C, 450 ⁰C for 1% ,2%, 3%, 5%, 5% metal loading respectively. For 1 % ruthenium loading catalyst, 16 % CO₂ conversion and 90 % methane selectivity achieved. For 1 % ruthenium loading catalyst, 16 % CO₂ conversion and 90 % methane selectivity achieved. For 2 % ruthenium loading catalyst, 24 % CO₂ conversion and 95 % methane selectivity achieved. For 3 % ruthenium loading catalyst, 51 % CO₂ conversion and 99 % methane selectivity achieved. For 4 % ruthenium loading catalyst, 55 % CO₂ conversion and 99 % methane selectivity achieved. For 5 % ruthenium loading catalyst, 55 % CO₂ conversion and 99 % methane selectivity achieved(Upham et al. 2011).

CHAPTER 3

MATERIAL & METHOD

3.1 Materials

In this study, three different types catalyst are prepared with a Sol-Gel method. These catalysts are containing three different metal oxides and 2 different metals as active sites. Aluminum and calcium mixed oxide, aluminum and magnesium mixed oxide, aluminum and barium mixed oxide with different percentage are used as supports for 1 wt % and 5 wt % nickel and ruthenium. The percentages of the oxides in mixed oxides are 70% - 30%, 50% - 50% and 20% - 80%. 500 °C of calcination temperature and 6 h of calcination time is used for all the catalysts.

For alumina based the catalyst supports, aluminum isopropoxide (AIP) is used as precursor. For calcium oxide, calcium nitrate tetrahydrate is used as precursor. For magnesium oxide, magnesium nitrate hexahydrate is used as precursor. For barium oxide, barium nitrate is used as precursor. Deionized water is used as solvent and nitric acid is used as peptizing agent in Sol-Gel method. Nickel (II) acetate is used as nickel precursor and Ruthenium (III) chloride is used as ruthenium precursor. All the properties of the chemicals that were used in the synthesis of catalysts are given in the Table 1 below.

Table 1: Properties of the Chemicals used in Procedure

Components	Molecular Weight	Density	Purity	Chemical Formula
Aluminum isopropoxide (AIP)	204.24	1.035	0.98	$\text{Al}(\text{C}_3\text{H}_7\text{O})_3$
Water	18.02	0.999	1	H_2O
Nitric Acid	63.01	1.4	0.65	HNO_3
Calcium Nitrate tetrahydrate	236.1489	1.82	0.99	$\text{CaNO}_3 \cdot 4\text{H}_2\text{O}$
Magnesium Nitrate hexahydrate	256.41	1.49	0.98	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Barium Nitrate	261.335	3.24	0.99	$\text{Ba}(\text{NO}_3)_2$
Nickel Acetate	176.79	1.744	0.99	$\text{C}_4\text{H}_6\text{NiO}_4$
Ruthenium (III) Chloride	207.43	3.11	0.99	RuCl_3

3.2 Methods

This section explains catalyst preparation, catalyst characterization and product analyses.

3.2.1. Catalyst Preparation

All of the nickel and ruthenium-based catalysts are prepared with modified Sol-Gel methods developed in Prof. Dr Erol Şeker's research group. For preparing Ni/Al₂O₃-CaO catalyst, first alumina sol was prepared. To prepare alumina sol, certain amount of aluminum isopropoxide and deionized water were mixed at 85 °C for 1 h. After 1 h, necessary amount of nitric acid was added and was mixed for additional 1 h. After preparing alumina sol, calcium nitrate tetrahydrate, which was calcium oxide precursor, was added to the mixture at the same temperature. After 30 min, nickel (II) acetate was added to the mixture. After 30 min, the mixture was evaporated to remove excess water to form nickel alumina calcium mix oxide gel. All gels were dried at 120 °C for 20 h. All the catalysts were calcined at 500 °C for 6 h. Then, all the catalysts were ground to 75 to 150 µm particle size.

For preparing Ni/Al₂O₃-MgO catalyst, first alumina sol was prepared in the same way used above. Magnesium nitrate hexahydrate, which was magnesium oxide precursor, was added to the mixture at the same temperature. After 30 min, a specified amount of nickel (II) acetate was added to the mixture. After 30 min, the mixture was evaporated to remove excess water to form nickel alumina magnesium mix oxide gel.

For preparing Ni/Al₂O₃-BaO catalyst, first alumina sol was prepared as before. Barium nitrate, which was barium oxide precursor, was added to the mixture at the same temperature. After 30 min, a specified amount of nickel (II) acetate was added to the mixture. After 30 min, the mixture was evaporated to remove excess water to form nickel alumina barium mix oxide gel.

For preparing Ru/Al₂O₃-CaO catalyst, first alumina sol was prepared as before. Calcium nitrate tetrahydrate was added to the mixture at the same temperature. After 30 min, specified amount of ruthenium (III) chloride was added to the mixture. After 30 min, the mixture was evaporated to remove excess water to form ruthenium alumina calcium mix oxide gel.

For preparing Ru/Al₂O₃-MgO catalyst, first alumina sol was prepared as before. Magnesium nitrate hexahydrate was added to the mixture at the same

temperature. After 30 min, a specified amount of ruthenium (III) chloride was added to the mixture. After 30 min, the mixture was evaporated to remove excess water to form ruthenium alumina magnesium mix oxide gel.

For preparing Ru/Al₂O₃-BaO catalyst, first alumina sol was prepared. Barium nitrate hexahydrate was added to the mixture at the same temperature. After 30 min, a specified amount of ruthenium (III) chloride was added to the mixture. After 30 min, the mixture was for evaporated to remove excess water to form ruthenium alumina barium mix oxide gel.

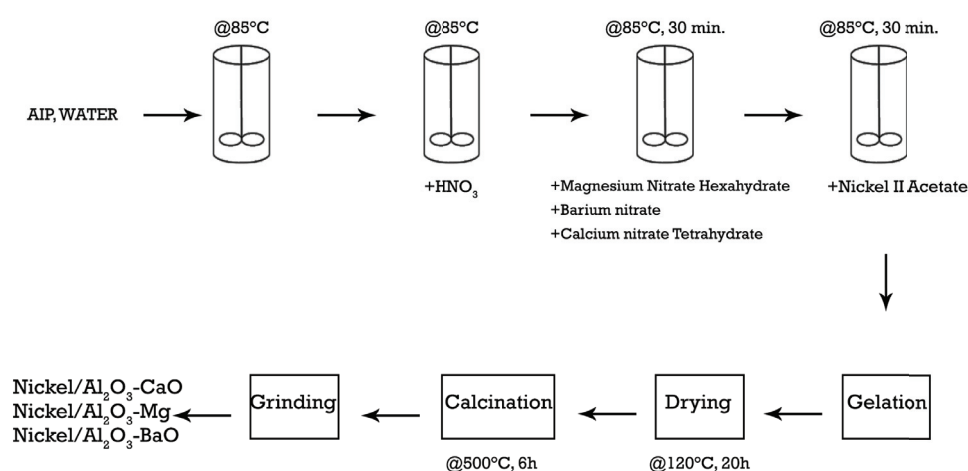


Figure 13: Experimental Procedure for Nickel based Catalyst

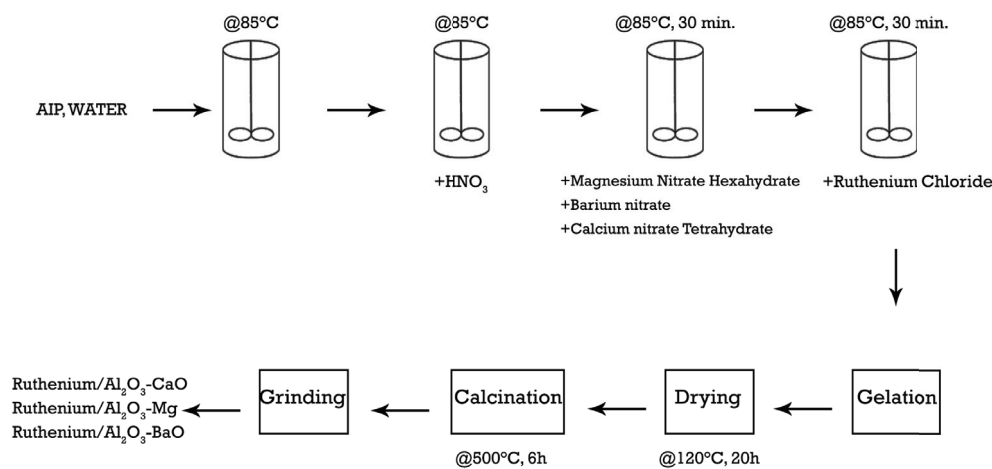


Figure 14: Experimental Procedure for Ruthenium based Catalyst

3.2.2 Catalyst Characterization

The catalysts were characterized with NH₃-TPD, X-Ray diffraction (XRD), Brunauer-Emmett-Teller (BET) method.

3.2.2.1 X-Ray Differentiation (XRD)

Crystallite sizes and crystalline phases were determined with using Philips X'Pert Pro X-Ray diffractometer which operated at 40 kV and 45 mA. Peak broadening and Scherrer equation were used for calculation of average crystallite size.

3.2.2.2 Brunauer-Emmett-Teller (BET)

Brunauer-Emmett-Teller (BET) was used to measure total specific surface area and pore size of the catalysts. Micromeritics Gemini V Surface area and Pore size Analyzer machine was used for analysis.

3.2.2.3 CO₂-Temperature Programmed Desorption (TPD)

CO₂-TPD method can be used for determining basic properties of solid surfaces. These basic properties are basicity, i.e. base amount, the nature of basic sites and strength. The basicity can be determined by number of moles of basic sites per unit amount of the catalysts. However, the nature of the basic sites, such Bronsted or Lewis, cannot be determined in this method. Working principles of this method is, in which carbon dioxide molecules adsorb to basic sites of the catalyst, desorb as the temperature is increased. The amount of the carbon dioxide molecules in the gas is measured. This amount and the temperature at which CO₂ desorbs give the basicity and basic strength of the catalysts.

3.2.3 Gas Product Analysis

The reactor exit gas products were analyzed with a GC equipped with TCD to measure amount of CO₂, CO and CH₄. Perkin Elmer Clarus 500 Gas Chromatography was used for analysis. The column is used between 50 to 250 °C.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Catalyst Characterization

In this study, prepared catalysts were characterized with XRD, BET and CO₂-TPD methods. With XRD method, the crystalline phases and average crystallite sizes can be found.

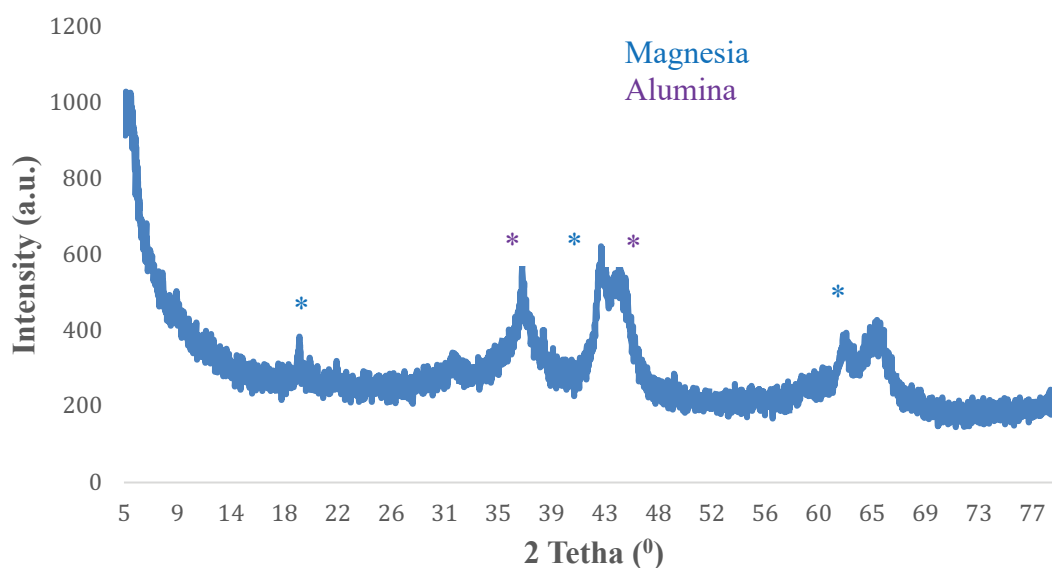


Figure 15: XRD Result for 5% Nickel loaded 70%-30% Aluminum-Magnesium mix oxide catalyst

Figure 15 shows the XRD pattern of the 70%-30% alumina magnesium oxide. Its nickel content was 5 wt.%. The highest peaks from XRD result shows that; the main crystalline phases were magnesia and aluminum oxide.

Figure 16 shows the XRD pattern of the catalyst with 50%-50% alumina magnesium oxide. Its nickel content was 5 wt.%. It was found that, the major peaks corresponded to magnesia and aluminum oxide.

Figure 17 shows the XRD pattern of 5 wt.% Ni on 20%-80% alumina magnesium oxide catalyst. The sharp peak is the diffraction of the magnesia. Besides, in Figures 15-17, no diffraction peak corresponding to nickel phase was observed; thus, indicating that the average crystallite size of Ni in all the catalysts given in Figures 15-17 was less than 5 nm.

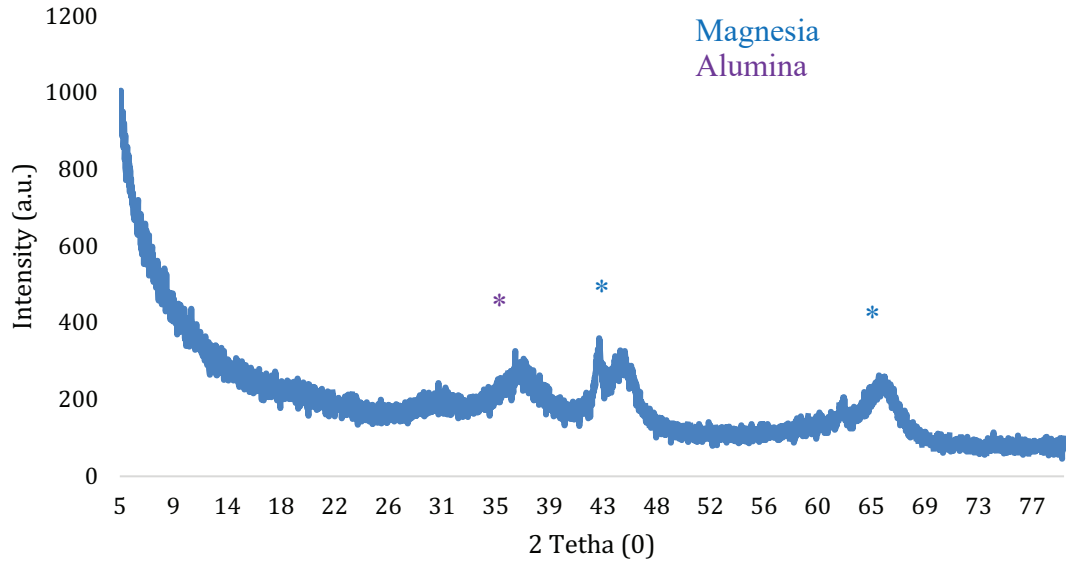


Figure 16: XRD Result for 5% Nickel loaded 50%-50 Aluminum-Magnesium mix oxide catalyst

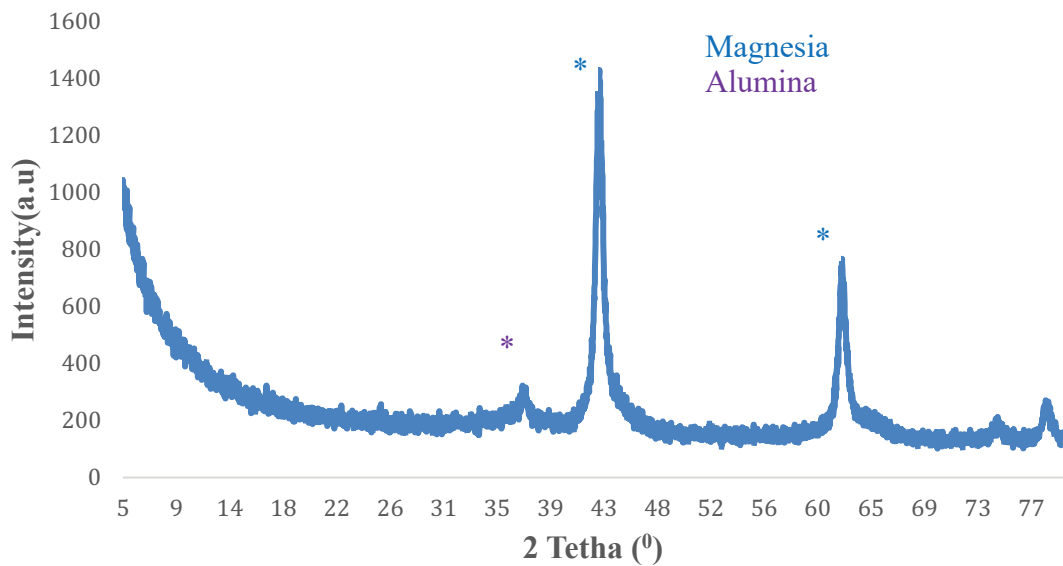


Figure 17: XRD Result for 5% Nickel loaded 20%-80 Aluminum-Magnesium mix oxide catalyst

This is plausible since it is well known that wide angle XRD is sensitive to crystallite sizes larger than 5 nm.

As seen in Figures 18-20, decreasing nickel content from 5 wt.% to 1 wt.% for the alumina-magnesia mixed oxides with the same composition as that of Figures 15-17 did not change crystalline phases present in all the catalysts.

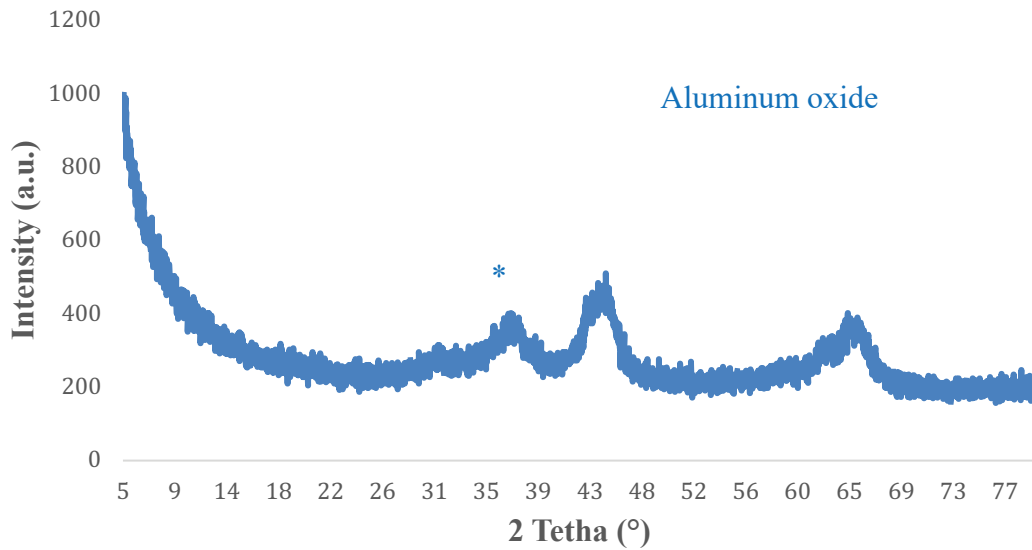


Figure 18: XRD Result for 1% Nickel loaded 70%-30 Aluminum-Magnesium mix oxide catalyst

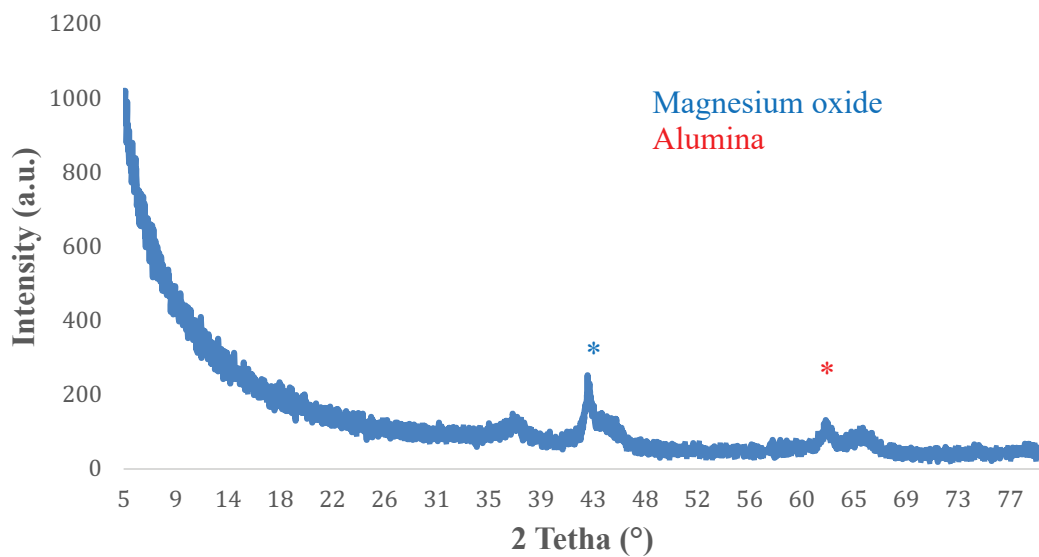


Figure 19: XRD Result for 1% Nickel loaded 50%-50 Aluminum-Magnesium mix oxide catalyst

In 1 wt.% Ni containing catalysts, there was no diffraction peak corresponding to Ni crystalline phase; thus, indicating that the crystallite size of Ni was less than 5nm. Figures 21-23 shows the XRD patterns of 5 wt.% Ni containing alumina and barium oxide catalysts with varying alumina and barium oxide compositions. Similar to alumina-magnesium oxide supported 5 wt.%Ni catalysts, there was no nickel and alumina crystalline phases.

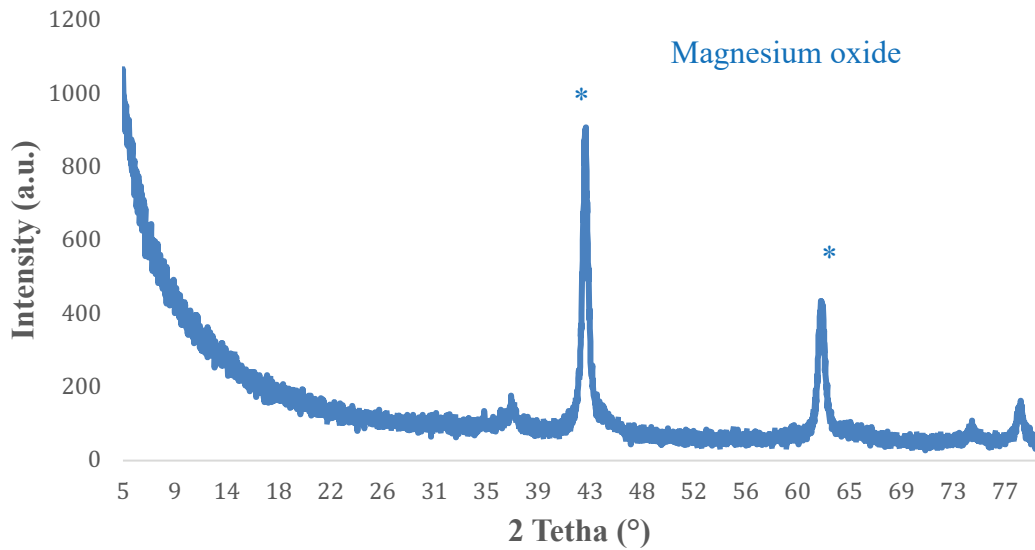


Figure 20: XRD Result for 1% Nickel loaded 20%-80 Aluminum-Magnesium mix oxide catalyst

which indicated that their crystallite sizes were less than 5 nm, but barium oxide crystalline phase was present and the sharpness of the peaks was increasing with barium oxide loading in all the catalysts; thus, indicating that the crystallite size of the barium oxide increased with increased barium oxide content.

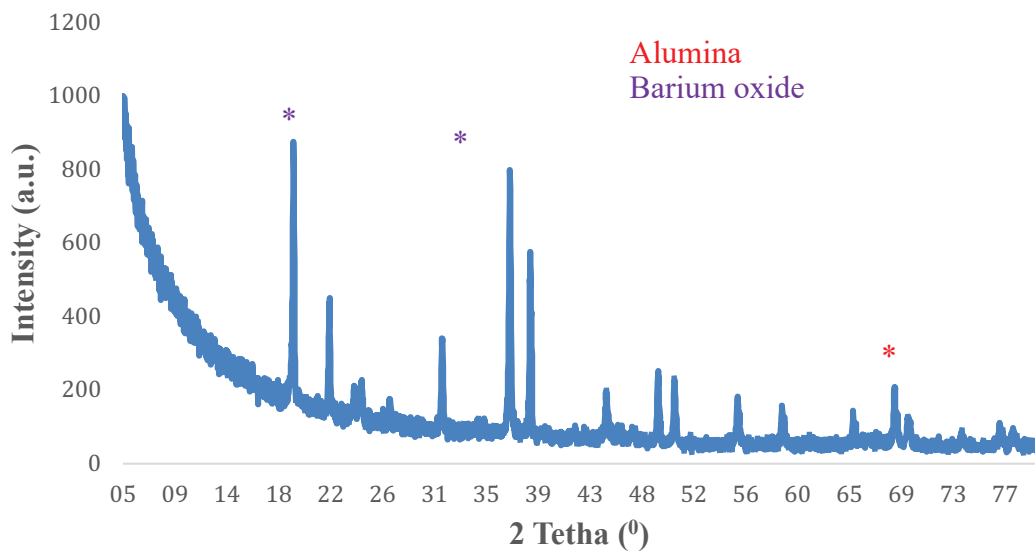


Figure 21: XRD Result for 5% Nickel loaded 70%-30 Aluminum-Barium mix oxide catalyst

As seen in Figure 24 and 25, diffraction patterns of 1% nickel loaded 70%-30% and 50%-50% aluminum barium mix oxide catalysts did not change as compared to 5% nickel loaded 70%-30% and 50%-50% aluminum barium mix oxide catalysts; thus, indicating that lowering nickel loading did not change the crystalline phases.

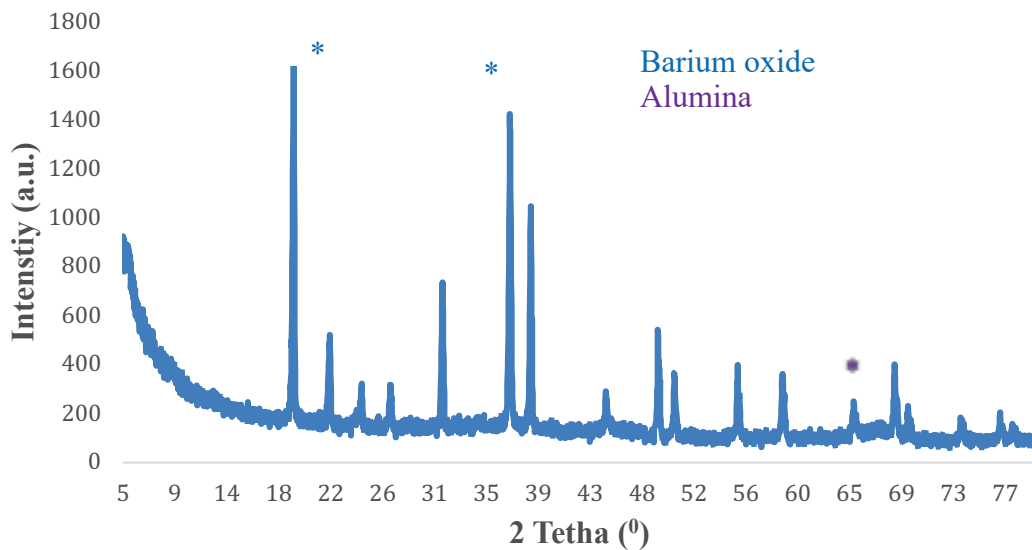


Figure 22: XRD Result for 5% Nickel loaded 50%-50 Aluminum-Barium mix oxide catalyst

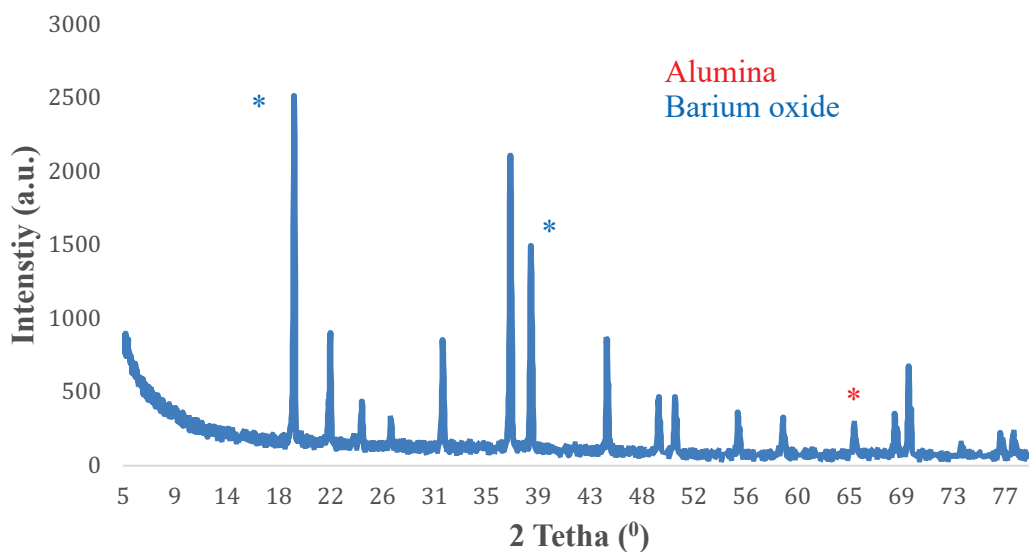


Figure 23: XRD Result for 5% Nickel loaded 20%-80 Aluminum-Barium mix oxide catalyst

In contrast to alumina-barium oxide supported nickel and alumina-magnesium supported nickel catalysts, there was no diffraction peaks, corresponding either alumina, calcium oxide and nickel, observed on alumina-calcium oxide supported nickel catalysts regardless of nickel loading and alumina/calcium oxide amounts as seen in Figures 26-28. This indicates that the average crystallite sizes for nickel, alumina and calcium oxide crystalline phases were less than 5 nm.

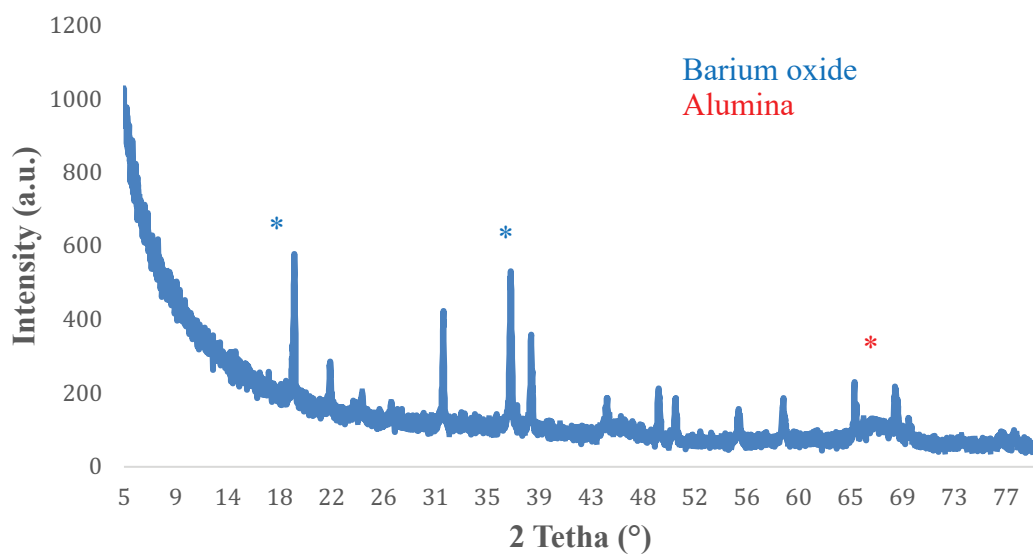


Figure 24: XRD Result for 1% Nickel loaded 70%-30 Aluminum-Barium mix oxide catalyst

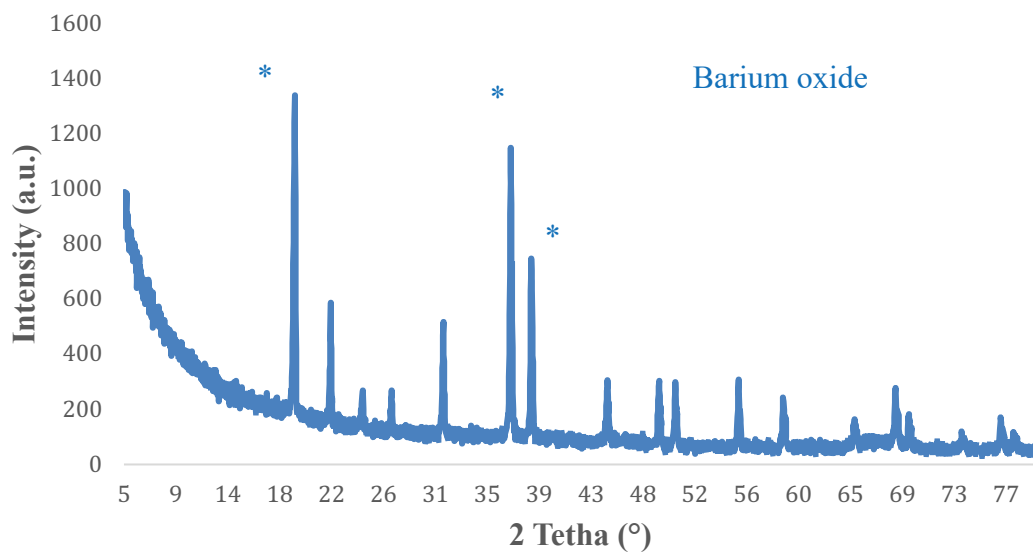


Figure 25: XRD Result for 1% Nickel loaded 50%-50 Aluminum-Barium mix oxide catalyst

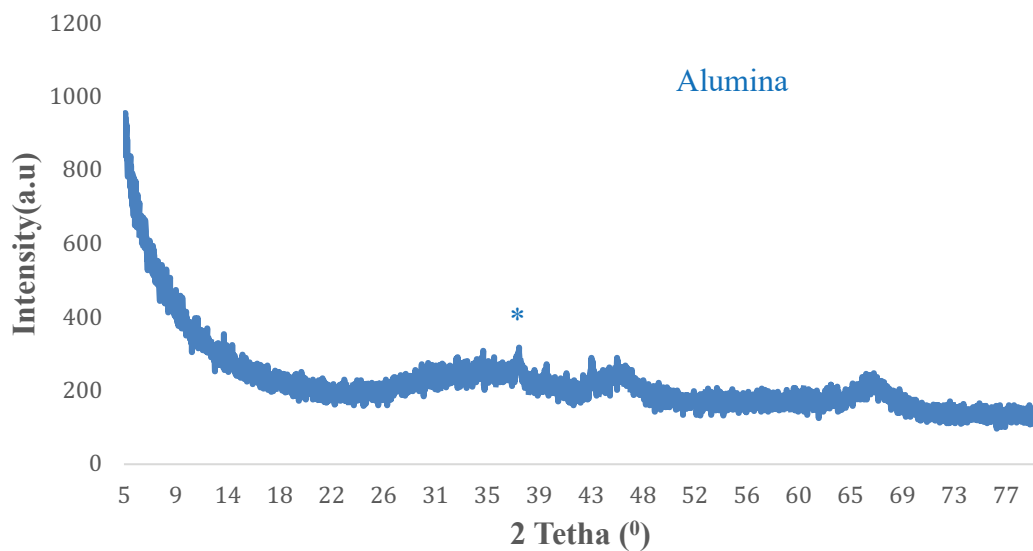


Figure 26: XRD Result for 5% Nickel loaded 70%-30 Aluminum-Calcium mix oxide catalyst

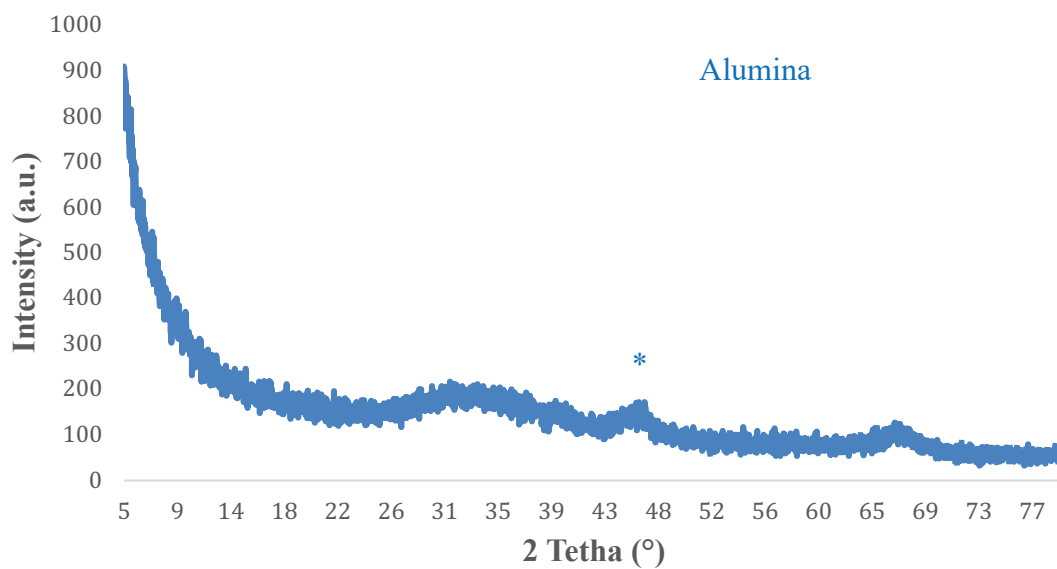


Figure 27: XRD Result for 1% Nickel loaded 70%-30 Aluminum-Calcium mix oxide catalyst

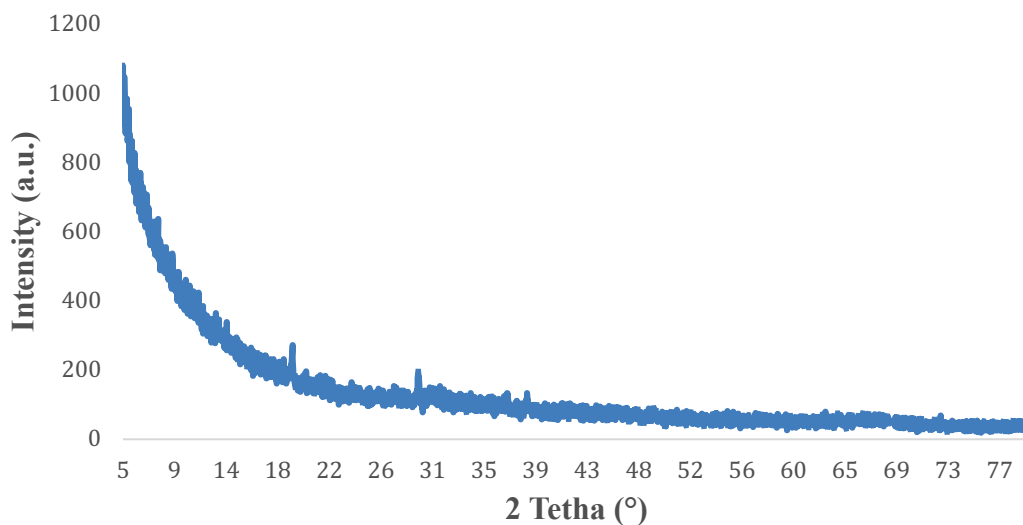


Figure 28: XRD Result for 1% Nickel loaded 50%-50 Aluminum-Calcium mix oxide catalyst

4.2 CO₂-TPD Characterization

A number of catalysts was selected for CO₂-TPD characterization to measure basicity and basic strength of the catalysts.

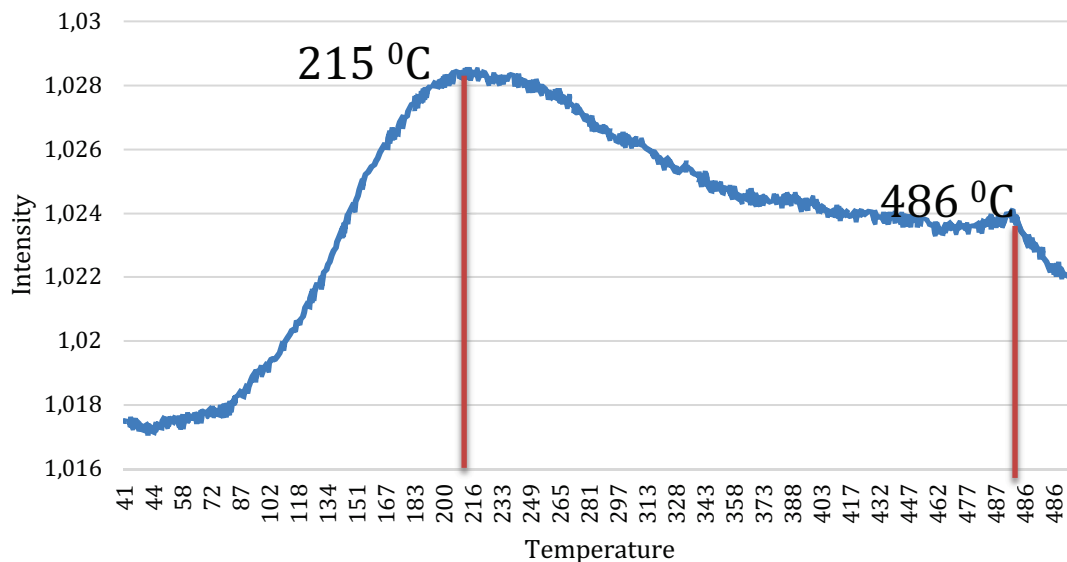


Figure 29: CO₂-TPD result of 1% Ni 50-50% alumina barium mix oxide catalyst

1%Ni 50-50% alumina barium mix oxide catalyst had basic sites with one medium and one weak basic strength, and the basicity of the catalyst was found to be 6.03 CO₂ area under the curve per g of the catalyst.

alumina magnesium mix oxide catalysts and the basic strengths of 1%Ni 50-50% alumina barium mix oxide 1%Ni 50-50% alumina magnesium mix oxide catalysts were similar but the basic strength of 0.5%Ru 50-50% alumina magnesium mix oxide catalyst was much lower than either of the catalysts.

4.3 The activity measurement of the selected catalysts

Table 2 shows the reaction conditions used in determining the catalytic activity and selectivity of the selected catalysts, such as 1% Ni 50-50 % Al₂O₃-MgO, 1% Ni 70-30 % Al₂O₃-MgO, 0.5 % Ru 70-30 Al₂O₃-MgO, 0.5 % Ru 70-30 Al₂O₃-BaO, 0.5 % Ru 70-30 Al₂O₃-CaO and 5% Ni 70-30 Al₂O₃-MgO.

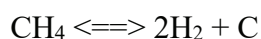
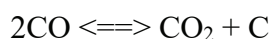
Table 2: Reaction Conditions for Catalysts

Catalyst	Inlet Condition (CO ₂ :H ₂)	Reaction Temperature (°C)	Catalyst Amount (mg)	Gas Sampling Time (min)
Inlet Composition	1:4.5			
1% Ni 50-50 % Al-Mg	1:4.5	300	50	45
1% Ni 70-30 % Al-Mg	1:4.5	460	50	45
1% Ni 50-50 % Al-Mg	1:4.5	50	50	0
1% Ni 50-50 % Al-Mg	1:4.5	460	50	45
Inlet Composition	1:4.5			
0.5 % Ru 70-30 Al-Mg	1:4.5	230	50	0
0.5 % Ru 70-30 Al-Mg	1:4.5	460	50	45
0.5 % Ru 70-30 Al-Ba	1:4.5	230	50	0
0.5 % Ru 70-30 Al-Ba	1:4.5	460	50	45
0.5 % Ru 70-30 Al-Ca	1:4.5	230	50	0
0.5 % Ru 70-30 Al-Ca	1:4.5	460	50	45
5% Ni 70-30 Al-Mg	1:4.5	230	50	0
5% Ni 70-30 Al-Mg	1:4.5	460	50	45

Catalyst amount was 50 mg and total inlet volumetric flow rate was kept at ~120 ml/min, corresponding to the space velocity of ~28,5000 h⁻¹. CO₂: H₂ ratio at the inlet was 4.5, and reaction temperatures were 300 °C and 460 °C and the exit gas stream of the reactor was analyzed at reaction time of 0 and 45 min.

Ruthenium-based catalysts showed the highest catalytic activity and selectivity to methane formation as seen Table 3. Among the ruthenium based catalysts, Al₂O₃-BaO mixed oxide supported 0.5% Ru catalyst showed the lowest methane and carbon monoxide formations whereas Al₂O₃-MgO and Al₂O₃-CaO mixed oxide supported 0.5% Ru produced the highest activity and the highest selectivity to methane and carbon monoxide. This seems to be due to the high basicity and low to medium basic strength and also to ruthenium metal. In other words, ruthenium based catalysts had higher activity toward both of the reverse water gas shift reaction and carbon dioxide methanation reaction.

For the same mixed oxide type and composition, nickel based catalyst showed the lowest activity and very low selectivity to carbon monoxide and no formation of methane. Besides, the color of the nickel based catalysts changed to carbon black color at the end of the reaction, which indicated that the carbon was deposited. This could happen through the following reactions:



This is plausible since nickel is well known for the breaking of carbon-carbon and carbon-oxide bonds.

Table 3: GC-TCD Results for Catalysts

Catalyst	CO ₂ Area (unreacted)	CO Area	CH ₄ Area
1% Ni 50-50 % Al-Mg	16511.5	23.4	0
1% Ni 70-30 % Al-Mg	197.5	0	0
1% Ni 50-50 % Al-Mg	16578	1054.2	10.4
1% Ni 50-50 % Al-Mg	14872.3	1159.4	0
0.5 % Ru 70-30 Al-Mg	25623	6220.9	5661.5
0.5 % Ru 70-30 Al-Mg	31918.3	8356.2	6503.4
0.5 % Ru 70-30 Al-Ba	20584	5	49.3
0.5 % Ru 70-30 Al-Ba	18366.1	2548.6	503.4
0.5 % Ru 70-30 Al-Ca	21913.4	9130.9	2305.3
0.5 % Ru 70-30 Al-Ca	28116.6	9993.6	1807
5% Ni 70-30 Al-Mg	16769	1446	5.5
5% Ni 70-30 Al-Mg	18377.5	557.2	1.4

CHAPTER 5

CONCLUSION

In this study, the effect of basicity of catalyst is investigated using different metal oxides supported Nickel and Ruthenium catalysts. The basic strength of catalysts was manipulated by using different types of metals and different composition of supports. In this study $\text{Al}_2\text{O}_3\text{-CaO}$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-BaO}$ supports were used to make supported nickel or ruthenium catalyst, which synthesized with a sol-gel method. Different mass ratios of supports were used such as; 100%, 70%/30%, %50/50%, 20%/80% for all the mixed oxides. For all the metal oxides, Nickel loadings are 1 %, 5% and Ruthenium loading is 0.5%. Calcination temperature was 500 °C and calcination time was 6 h. All the catalysts were used in methanation reaction with conditions varies between 300 or 500 °C, inlet ratio of $\text{CO}_2/\text{H}_2 \sim 1/5$ and GSHV 5000h^{-1} . The gas products were analyzed using GC and the catalysts were characterized using XRD, $\text{NH}_3\text{-TPD}$ and BET.

Nickel load selected as 1%, magnesium supported catalysts' the main crystallites were aluminum oxide and magnesium oxide for 30%, 50%, 80; respectively. Calcium supported catalyst had had alumina and calcium oxide crystallites for 30% and 50%, respectively. Barium supported catalysts had had alumina and barium mix oxide crystallites for 30% and 50% loadings, respectively. For 5% Nickel loaded 70-30% alumina magnesia mix oxide catalyst, magnesia and alumina crystallites were found. Ruthenium-based catalysts showed the highest catalytic activity and selectivity to methane formation. Among the ruthenium based catalysts, $\text{Al}_2\text{O}_3\text{-MgO}$ and $\text{Al}_2\text{O}_3\text{-CaO}$ mixed oxide supported 0.5% Ru produced the highest activity and the highest selectivity to methane and carbon monoxide. This seems to be due to the high basicity and low to medium basic strength and also to ruthenium metal. In other words, ruthenium based catalysts had higher activity toward both of the reverse water gas shift reaction and carbon dioxide methanation reaction.

For the same mixed oxide type and composition, nickel based catalyst showed the lowest activity and very low selectivity to carbon monoxide and no formation of

methane. Besides, the color of the nickel based catalysts changed to carbon black color at the end of the reaction, which indicated that the carbon was deposited.

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