DIMETHYL ETHER PRODUCTION FROM METHANOL OVER SILICA-ALUMINA CATALYSTS

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ABSTRACT

DIMETHYL ETHER PRODUCTION FROM METHANOL OVER SILICA-ALUMINA CATALYSTS

This study aims to investigate the effect of acidic properties of acidic catalysts on the activity, which is required to produce dimethyl ether from methanol. In this study, silica-alumina (SiO_2/Al_2O_3) catalysts with different compositions which are 25/75 wt.%, 50/50 wt.%, 75/25 wt.%, and 3 different calcination temperatures which are 500°C, 700°C, and 900°C were synthesized by the sol-gel method for the methanol dehydration to dimethyl ether reaction. In the further stages of the study, some changes were made in the catalyst formulations of the most active and the least active catalysts in terms of catalytic performance to modify acidic properties. In this regard, the peptizer acid of silica-alumina catalysts was changed from HNO_3 to H_2SO_4, or 0.1 g of ZSM-5 zeolite was added to the silica-alumina sol mixture step. The NH_3-TPD analysis was used to understand the acidic properties of all synthesized SiO_2/Al_2O_3 catalysts. The reaction temperatures were 300°C and 400°C for both 30 min.

The study has shown that there was a decrease in the acidity of the catalysts calcined at 900°C is observed. The activity of 75%SiO_2-25%Al_2O_3 catalyst decreases significantly as the calcination temperature increases. The activities of all catalysts calcined at 500°C are close to each other, whereas there is a big difference in activity between 25%SiO_2-75%Al_2O_3 and 75%SiO_2-25%Al_2O_3 catalysts calcined at 900°C. As evidence of the NH_3-TPD results, 25/75 wt.% catalyst calcined at 900°C was the most active catalyst with approximately 97% methanol conversion, while 75/25 wt.% catalyst calcined at 900°C was the least active catalyst with 63% conversion at 400°C. The 50/50 wt.% catalyst calcined at 900°C is also a very active catalyst with over 90% conversion. While sulfuric acid and/or zeolite exchange increased the performance of the least active catalyst, it did not reveal much difference in the most active catalysts. In addition, the addition of ZSM-5 zeolite increased the acidic strength of the catalysts. All synthesized catalysts are active for methanol dehydration. The DME selectivity for all catalysts is approximately 100%.

ÖZET

SİLİKA-ALÜMİNA KATALİZÖRLERİ ÜZERİNDE METANOLDEN DİMETİL ETER ÜRETİMİ

Bu çalışmanın amacı, metanolden dimetil eter üretmek için gerekli olan asidik katalizörlerin asidik özelliklerinin aktivite üzerindeki etkisini araştırmaktır. Bu çalışmada, metanol dehidrasyonuyla dimetil eter sentezlemek için farklı oranlarda ağırlıkça 25/75, 50/50 ve 75/25 olmak üzere çeşitli kompozisyonlarda; 500°C, 700°C ve 900°C olmak üzere 3 farklı kalsinasyon sıcaklığında silika-alümina (SiO_2/Al_2O_3) katalizörleri sol-jel yöntemiyle sentezlenmiştir. Çalışmanın ilerleyen aşamalarında, asidik özellikleri modifiye etmek için katalitik performans açısından en aktif ve en az aktif katalizörlerin katalizör formülasyonlarında bazı değişiklikler yapılmıştır. Bu bağlamda, silika-alümina katalizörlerinin peptitleştirici asiti HNO_3'ten H_2SO_4'e değiştirilmiştir ve/veya silika-alümina sol karışımına 0.1 g ZSM-5 zeoliti eklenmiştir. Sentezlenen tüm SiO_2/Al_2O_3 katalizörlerinin asidik özelliklerini anlamak için NH_3-TPD analizi kullanılmıştır. Reaksiyon sıcaklıkları 300°C ve 400°C'dir.

Çalışma, 900°C'de kalsine edilen katalizörlerin asiditelerinde bir azalma olduğunu göstermiştir. Kalsinasyon sıcaklığı arttıkça %75SiO_2-25%Al_2O_3 katalizörünün aktivitesi önemli ölçüde azalmıştır. 500°C'de kalsine edilen tüm katalizörlerin aktiviteleri birbirine yakınken, 900°C'de kalsine edilen %25SiO_2-75%Al_2O_3 ve %75SiO_2-25%Al_2O_3 katalizörleri arasında aktivite açısından büyük fark olduğu görülmüştür. NH_3-TPD sonuçlarının kanıtı olarak, 900°C'de kalsine edilmiş ağırlıkça 25/75 katalizörü 400°C reaksiyon sıcaklığında yaklaşık %97 metanol dönüşümü ile en aktif katalizör iken 900°C'de kalsine edilmiş ağırlıkça 75/25 katalizörü %63 dönüşümle en az aktiftir. Ayrıca 900°C'de kalsine edilen ağırlıkça 50/50 katalizörü %90'ın üzerinde dönüşümle bir diğer en aktif katalizördür. Daha sonra bu katalizörler üzerinde yapılan sülfürik asit ve/veya zeolit modifikasyonu, en az aktif katalizörün performansını arttırırken en aktif katalizörlerde çok fazla bir fark ortaya koymamıştır. Ek olarak, ZSM-5 zeolitinin ilavesi, katalizörlerin asidik gücünü arttırmıştır. Sentezlenen tüm katalizörler metanol dehidrasyonu için aktiftir. Tüm katalizörler için dimetil eter seçiciliği yaklaşık %100'dür.

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CHAPTER 1

INTRODUCTION

The world population's growth rate is nearly 1.05% per year and it is estimated that the human population has been increasing at about 81 million people per year (The World Bank, 2020). Meanwhile, the rapid world population growth has been increasing human activities such as transportation, industrialization to meet the energy demand of the global economy. This situation has brought with the excessive use of energy resources.

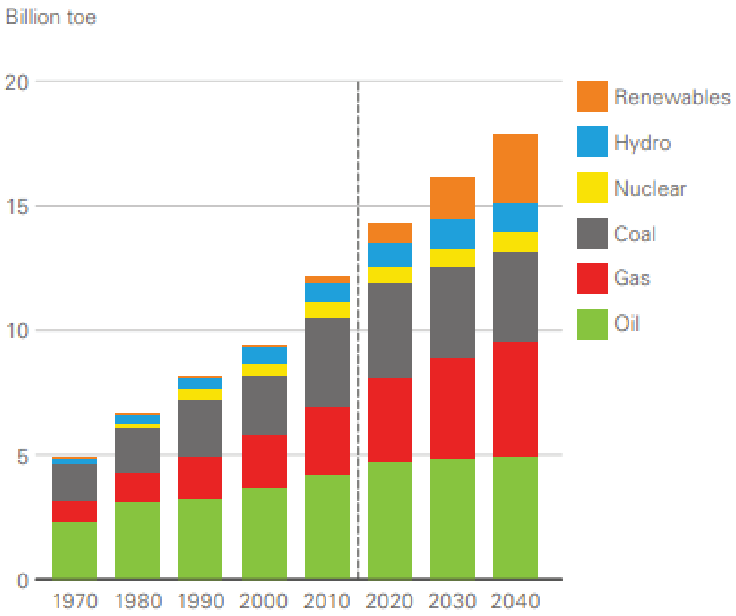


Figure 1.1. Energy consumption and energy demand by fuels from 1970 to 2040

(Source: BP Energy Outlook, 2019)

It can be seen from Figure 1.1 that the energy demand as well the energy consumption have been increasing worldwide between 1970 and 2040. It is reported that global energy consumption has been dominated by coal, oil, and gas at about 84% in 2019 (BP Statistical Review of World Energy, 2020). Although renewables show a rapid development, the continuation of the large rate of fossil fuel usage has been threatening the world in terms of pollution and so climate change year by year.

The use of fossil resources causes air pollution by releasing volatile organic compounds (VOCs), NOx, SOx, particulate matter (PM), and greenhouse gases (GHGs)

(Shih et al., 2018). Greenhouse gases (GHGs) compromise water vapor, methane, nitrous oxide, carbon dioxide, ozone-destructive chlorofluorocarbons (CFCs), and some others. These released gases cause to increase in the vital temperature of the Earth by capturing the infrared radiation coming from the Sun and reflected from the Earth's surface. This process is called the greenhouse gas effect. The excessive CO_2 emissions in greenhouse gases have a radiative effect rate of 64% to contribute to the greenhouse gas effect (Olah et al., 2018, p. 91). Therefore, it is necessary to focus on CO_2 emissions.

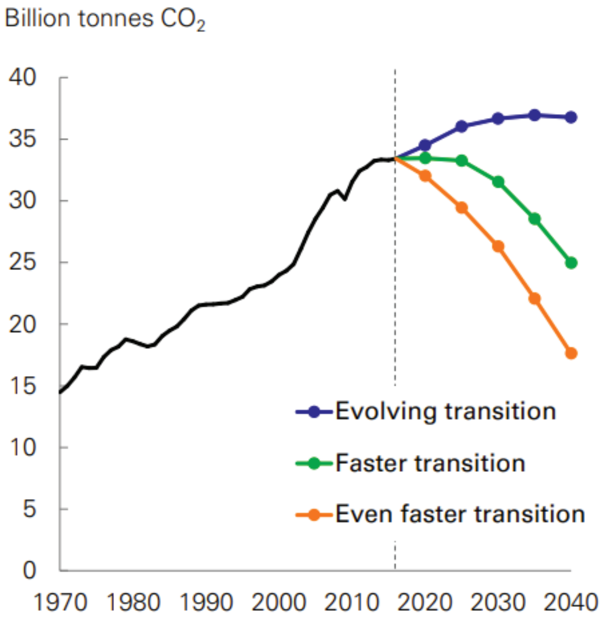


Figure 1.2. CO_2 emissions worldwide and some scenarios

(Source: BP Energy Outlook, 2018)

Throughout industrialization history, the concentration rate of anthropogenic (i.e., human-based) CO_2 emissions in the atmosphere has increased by 48% compared to the years of the 1750s (Olah et al., 2018, p. 88). Statistically, CO_2 emissions increased from 18.0 billion tonnes (bt) in 1978 to 33.7 bt in 2018 (Kober et al., 2020) and it is expected to be 36 bt in 2025 (Global Energy Outlook, 2019) because of burning fossil fuels. However, depending on the increase in the tendency of carbon-neutral ways, the sustainable development scenarios have predicted that CO_2 emissions will be decreased by approximately 45% until 2040 (BP Energy Outlook, 2019) and hopefully net-zero in 2070 (Global Energy Outlook, 2019).

To eliminate or alleviate CO_2 emissions, the recycling of the CO_2 processes has been researched to find the cleanest way to meet the growing energy demand. Through this process, a renewable energy source is provided an alternative fuel that takes place in a carbon-neutral way. These clean alternative fuels can be methanol (MeOH) and/or dimethyl ether (DME) through the chemical reduction of CO_2 with hydrogen (Olah et al., 2009). Compared to diesel fuel or even methanol, DME has attracted attention as fuel with its environmentally benign characteristics and superior fuel properties.

Historically, dimethyl ether (DME) has gained attention with its use as an aerosol propellant by AkzoNobel in 1963, has increased its research and development activities in the 1970s by Amoco. Dimethyl ether (DME), which started to be tested in diesel engines in the 1980s, was first tested in buses by Volvo in the 1990s. In the same years, Haldor Topsoe, Amoco and Navistar International Corporation started to produce DME from methanol on a large scale. In the 2000s, the International DME Association was established by the China DME Association (CDA), Korea DME Forum (KDF), and Japan DME Forum (JDF). Nowadays, China is the largest producer of DME for LPG blending. While the DME market size in China was $3.9 billion in 2018, this amount is estimated to be $9.6 billion by 2025. The worldwide size of the DME market is expected to reach $10.8 billion by 2025 (Mondal & Yadav, 2019; Global Market Insights, 2019).

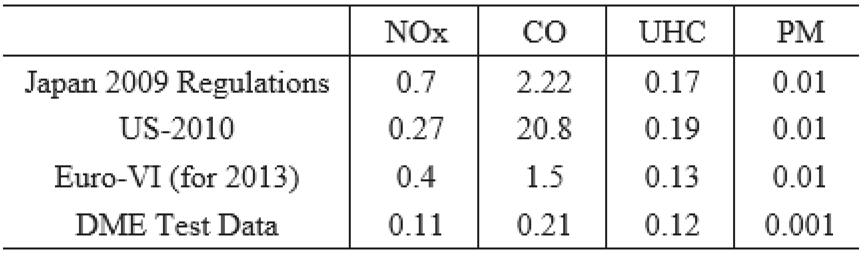
1.1. Features of Dimethyl Ether (DME)

Dimethyl ether, DME (IUPAC: methoxymethane) is the simplest form of ethers. It is an environmentally benign liquefied gas that is noncarcinogenic, colorless, non-toxic, non-corrosive, nearly odorless, not harmful to human health (Azizi et al., 2014) and it has clean-burning characteristics. DME can be used as a diesel fuel substitute, electric power generation, cooking fuel, non-destructive aerosol propellant to replace CFCs, and it is an intermediate to produce highly valuable chemicals like light olefins (Olah et al., 2009; Olah et al., 2018, p. 233).

DME does not harm the environment and does not contribute significantly to global warming. When the global warming potential of DME is examined, the lifetime DME in the troposphere of the Earth is only 5 days, and the global warming potential (GWP) is only 0.3 in 100 years whereas the global warming potential of methane (CH_4) is 21 and nitrous oxide (N_2O) is 310 in 100 year-time-horizon (Park & Lee, 2014).

The emission data for nitric oxide (NOx), carbon monoxide (CO), unburned hydrocarbons (UHC), and particulate matter (PM) produced by DME when used as fuel in heavy-duty trucks are shown in Table 1.1. Accordingly, DME emissions are significantly lower than required by Japan, US, and Euro-VI regulations.

Table 1.1. DME emission data in trucks, gms/kwhr (Fleisch et al., 2012)



	NOx	CO	UHC	PM
Japan 2009 Regulations	0.7	2.22	0.17	0.01
US-2010	0.27	20.8	0.19	0.01
Euro-VI (for 2013)	0.4	1.5	0.13	0.01
DME Test Data	0.11	0.21	0.12	0.001

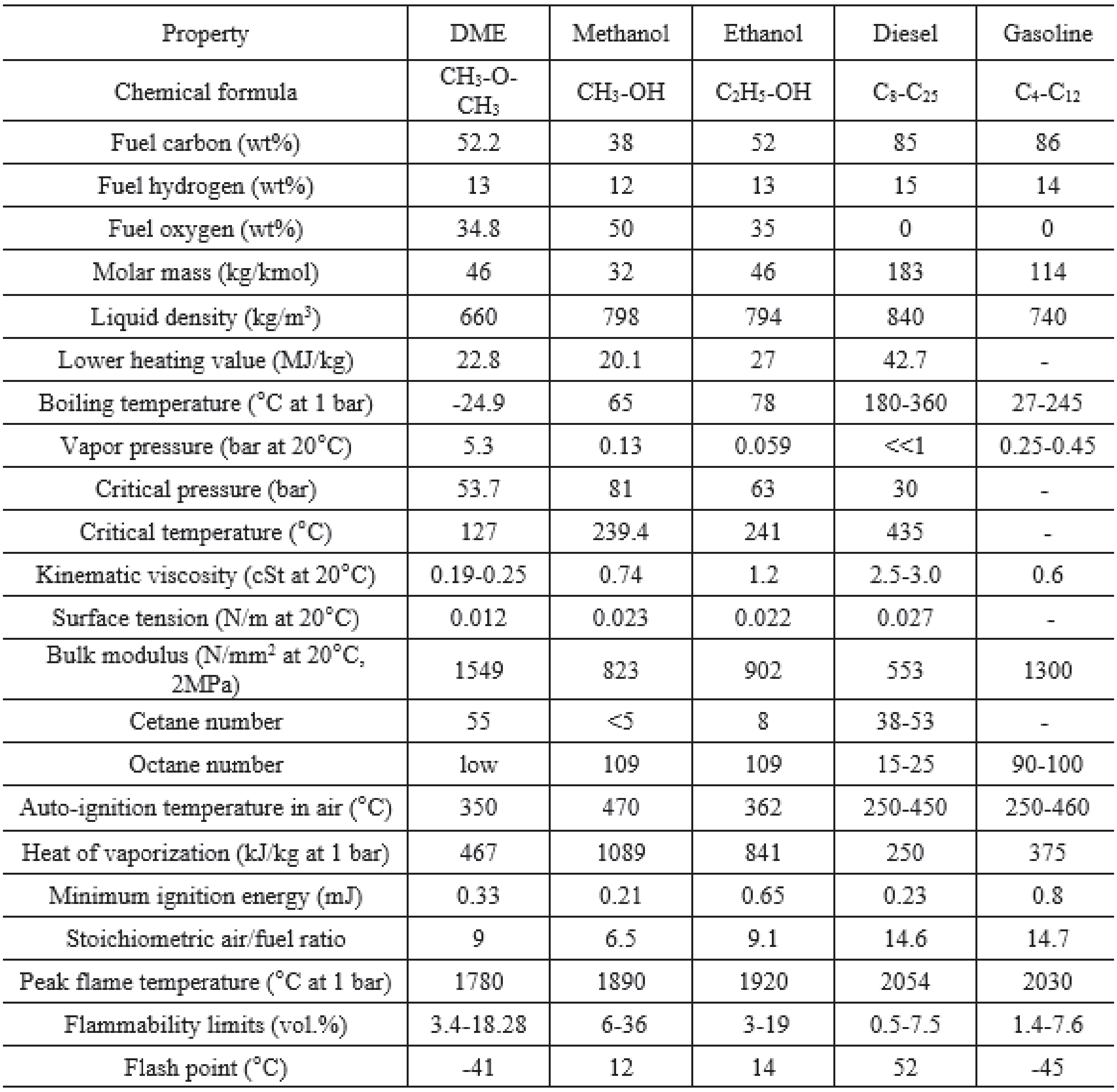
As fuel properties of DME can be seen in Table 1.2, the boiling point of DME is quite low which is -24.9°C and DME is a gas form under ambient conditions. However, DME is usually stored as a liquid such as liquefied petroleum gas (LPG) in pressurized tanks. Stored DME does not create explosive peroxides and ensures safe storage and usage, unlike the other higher ethers such as diethyl ether (Olah et al., 2009; Olah et al., 2018, p. 233). In terms of fuel properties, the low boiling point of DME in the cylinder of the compression ignition engine ensures better atomization, rapid evaporation, therefore it improves combustion. The lower boiling point also ensures an easy start of the engine even when the weather is cold.

A lower auto-ignition temperature of DME affects the combustion and it gets a higher cetane number for DME. The high cetane number is to be desirable for efficient operation for a diesel engine. Because the higher cetane number ends up with obtaining effortless ignition, more finished combustion, and reduced exhaust gas emissions. Moreover, engine noise and fuel consumption are also reduced with a high cetane number (Catizzone, 2017). The cetane number of DME is 55, which is substantially higher than the other compared fuels in Table 1.2.

DME is an absence of carbon-carbon bonds in its molecular structure. Thus, it releases not significantly smoke or soot pollutants and low concentration of particulate matter. As a disadvantage, DME has high oxygen content results in lower calorific value. Besides, lower LHV (lower heating value) of DME brings about a longer injection period and more injected volume for DME to deliver the same amount of energy has already provided by diesel fuels.

Given a further disadvantage, if diesel fuel is to be entirely replaced by DME, the engine configuration will have to be tailored for DME. The low viscosity and lubricity of DME can lead to fuel leakage and wear in pumps and fuel injectors. Therefore, special gaskets are needed to prevent leakage, and additives are needed to improve lubricity. Also, DME can act as a solvent to some organic compounds in the materials of the engine, causing incompatibility with elastomer or plastic materials. For this reason, a careful material selection should be made in diesel engines when DME is used as fuel (Valera & Agarwal, 2019, p.13; Catizzone, 2018; IEA-AMF, n.d.).

Table 1.2. Comparison of properties of dimethyl ether (DME) and other fuels (Valera & Agarwal, 2019, p.12).



Property	DME	Methanol	Ethanol	Diesel	Gasoline
Chemical formula	CH_3-O-CH_3	CH_3-OH	C_2H_5-OH	C_8-C_{25}	C_4-C_{12}
Fuel carbon (wt%)	52.2	38	52	85	86
Fuel hydrogen (wt%)	13	12	13	15	14
Fuel oxygen (wt%)	34.8	50	35	0	0
Molar mass (kg/kmol)	46	32	46	183	114
Liquid density (kg/m^3)	660	798	794	840	740
Lower heating value (MJ/kg)	22.8	20.1	27	42.7	-
Boiling temperature (°C at 1 bar)	-24.9	65	78	180-360	27-245
Vapor pressure (bar at 20°C)	5.3	0.13	0.059	<<1	0.25-0.45
Critical pressure (bar)	53.7	81	63	30	-
Critical temperature (°C)	127	239.4	241	435	-
Kinematic viscosity (cSt at 20°C)	0.19-0.25	0.74	1.2	2.5-3.0	0.6
Surface tension (N/m at 20°C)	0.012	0.023	0.022	0.027	-
Bulk modulus (N/mm^2 at 20°C, 2MPa)	1549	823	902	553	1300
Cetane number	55	<5	8	38-53	-
Octane number	low	109	109	15-25	90-100
Auto-ignition temperature in air (°C)	350	470	362	250-450	250-460
Heat of vaporization (kJ/kg at 1 bar)	467	1089	841	250	375
Minimum ignition energy (mJ)	0.33	0.21	0.65	0.23	0.8
Stoichiometric air/fuel ratio	9	6.5	9.1	14.6	14.7
Peak flame temperature (°C at 1 bar)	1780	1890	1920	2054	2030
Flammability limits (vol.%)	3.4-18.28	6-36	3-19	0.5-7.5	1.4-7.6
Flash point (°C)	-41	12	14	52	-45

To overcome to some extent engine-configurational disadvantages of DME and polluter diesel fuels, DME can be easily blended with diesel fuel in any ratio. Thus, the specific benefits of each fuel can be used. With the blended fuel, the desired physical properties of each fuel and the cleaner-burning ability of DME are obtained (Ying et al., 2008). In a study using a ratio of 30% DME/70% LPG, the CO_2 emissions of the gasoline engines were found to be 30% cleaner (IDA Fact Sheet No. 2, 2010, as cited in Styring et al., 2021).

The objective of this thesis is to investigate the effect of acidity and acidic strength on the activity of the catalysts to be used for DME production by a methanol dehydration reaction. For this purpose, SiO_2/Al_2O_3 acidic catalysts with different compositions as 25/75 wt.%, 50/50 wt.%, 75/25 wt.% and at different calcination temperatures which are 500°C, 700°C and 900°C were produced by sol-gel method. According to the catalytic performance of these catalysts, the contents of the most active and the least active ones were then updated with the addition of H_2SO_4 and/or ZSM-5 zeolite, then acidic properties and activities were investigated. The dehydration reactions take place at 300°C and 400°C for 30 min. under atmospheric pressure. For the catalyst characterization, the NH_3-TPD technique was used. Product analysis was done by using the GC-MS method.

This thesis consists of 5 chapters. In the first part, global energy consumption, the effects of fossil fuel usage on the climate, and the features of dimethyl ether (DME) as a clean fuel are mentioned. In the second chapter, studies on methanol dehydration and catalysts used in DME production are given. In Chapter 3, the materials and methods used in this study are explained. In Chapter 4, the results of the analysis and the outputs are discussed. Finally, the conclusion of this study is given in Chapter 5.

CHAPTER 2

LITERATURE SURVEY

2.1. Methanol Dehydration

Conventionally, dimethyl ether (DME) is obtained by the catalytic bimolecular dehydration of methanol. Dehydration of methanol, the primary alcohol (R-OH), requires an acidic catalyst to protonate the hydroxyl group of the alcohol to convert it into a well leaving group (Wade, Jr., 2013, p.487). Acidic properties such as acidity and acidic strength of the catalyst used in the dehydration reaction significantly affect the reaction rate and the selectivity of the reaction. Acidity is the amount of acid sites per unit weight of the catalyst and is obtained by measuring the amount of a base that reacts with the solid acid. Acidic strength is defined as the ability of the catalyst surface to convert an adsorbed neutral base into its conjugate acid. The acidic properties of the catalyst can be changed by parameters such as the composition of the catalyst and the calcination temperature (Tanabe, 1989). Thus, the acidic properties required to produce DME from methanol are obtained.

It is preferred that the methanol dehydration to dimethyl ether reaction, which is an exothermic reaction, be at lower temperatures. It is noted that undesired by-products like formaldehyde and/or a significant amount of coke formation are observed in a certain time on stream at high temperatures (Azizi et al., 2014).

The mechanism of methanol dehydration may differ from study to study. It was found that the mechanism of methanol dehydration to DME includes two adjacent sites which are acidic site (H^+) and adjacent basic site (O_2^-) on the catalyst surface as Langmuir–Hinshelwood kinetic model. On the acidic site, methanol is protonated to form $[CH_3 \cdot OH_2]^+$, then it is rapidly converted to form $[CH_3]^+$ and H_2O. On the adjacent basic site, one methanol molecule is transformed to form $[CH_3O]^-$ and $[OH]^-$. Consequently, DME (CH_3OCH_3) may be synthesized by combining two activated species which are $[CH_3]^+$ and $[CH_3O]^-$ (Bandiera & Naccache, 1991). In another study, the Eley-Rideal kinetic model is proposed for methanol dehydration reaction wherein one molecule of methanol was adsorbed on the acidic site of the catalyst as the other reacting molecule remained in the bulk phase (Pääkkönen et al., 1998).

2.2. Synthesis of Dimethyl Ether (DME)

Dimethyl ether (DME) can be produced by either an indirect synthesis method or a direct synthesis method (Figure 2.1). The indirect synthesis method, called methanol to dimethyl ether (MTD), is a conventional method wherein methanol and DME production takes place in a two-stage process. Methanol can be produced by synthesis gas or CO_2 obtained from coal, oil, natural gas, or biomass over Cu/Zn-based catalysts by hydrogenation with increasing pressure and decreasing temperature. In the following stage, DME is synthesized by bimolecular solid-acid-catalyzed dehydration of methanol. In the dehydration reaction, two moles of methanol convert into DME and water (Eq. 1). Because of the nature of reversible methanol dehydration reaction, it is possible that methanol goes through the desired MTD reaction and it also tends to form backwardly its components (Eq. 2) during the dehydration reaction. In such cases mentioned, methanol synthesis can also be performed under high-pressure conditions with the catalysts used as well as dimethyl ether production.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H^{o}_{298K} = -23.5\ \text{kJ/mol} \qquad \text{(Eq. 1)}$$

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad \Delta H^{o}_{298K} = -90.4\ \text{kJ/mol} \qquad \text{(Eq. 2)}$$

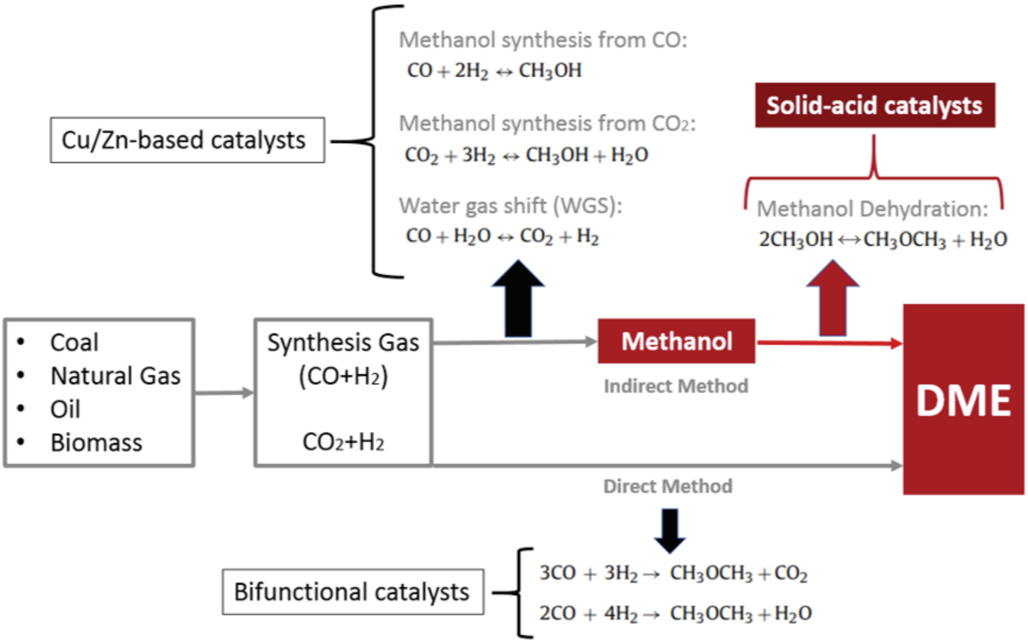


Figure 2.1. DME production route

In the direct synthesis method, methanol and DME synthesis take place in a single stage over bifunctional catalysts. In this process, bifunctional (i.e., hybrid) catalysts combine the requirements of methanol synthesis catalyst and methanol dehydration catalyst. The two overall reactions depending on whether the water-gas shift reaction is considered can be seen in Figure 2.1.

The water-gas shift reaction in the methanol synthesis is an exothermic, reversible chemical reaction, and in this way, the water formed by methanol synthesis can be removed from the system. Thus, it results in the equilibrium composition shifting to the desired direction during production. Also, the reversible WGS reaction plays an important role in adjusting the CO/H_2 ratio, which determines the raw gas quality, to the levels required for fuel or chemical production. Since the synthesis gas composition produced from different sources is variable as CO-free, CO-rich, or H_2-rich synthesis gas. (Bertau et al., 2014, p.224).

In any production route, methanol dehydration to DME reaction takes place over acid sites on the catalyst and it is necessary to obtain proper acidic properties over solid-acid catalysts in the investigations.

2.3. Catalysts for Methanol to Dimethyl Ether (MTD) Reaction

Methanol dehydration to DME takes place over solid-acid catalysts. As a drawback, the formation of water in the dehydration reaction would suppress the activity of the catalyst. Also, the acidic strength of the catalyst can cause the formation of undesirable by-products, thereby reducing the selectivity and yield of the DME. Brønsted and/or Lewis acidic nature is responsible for the formation of DME on the catalyst. It is essential to develop active, selective, and stable dehydration catalysts that have high resistance to water produced by a dehydration reaction and coke formation on the catalyst surface. In the literature, there are so many studies about γ-alumina and H-ZSM-5 as dehydration catalysts due to easy accessibility and adjustability. Differently, the performance of Al impregnated SBA-15 (i.e., mesoporous structure aluminosilicate), aluminophosphate and silico-aluminophosphate molecular sieves, and Al-HMS (i.e., Al incorporated hexagonal mesoporous silica) have been investigated for methanol dehydration to DME reaction.

Raoof et al. (2008) studied the methanol dehydration reaction by using γ-alumina and tested it in an adiabatic fixed-bed reactor with 0.018 m inner diameter by using an 8.2 g catalyst at the operating temperature range between 233-303°C under pure methanol stream at 2.02 cm^3/min in the reactor. They reported that methanol conversion was insignificant below 230°C but as the temperature was raised to 250°C, methanol conversion reached 85%. For 30 hours of experimentation, the activity of the catalyst was almost unchanged. As a feed, 80% methanol and 20% water mixture were fed into the reactor to see the effect of water on the deactivation of the catalyst. Water with methanol combination in the feed stream caused faster deactivation of γ-alumina compared to using pure methanol as feed. The water has a blocking effect on the active sites as it can be adsorbed by the Lewis acid sites of the catalyst.

As a solution for the water blocking effect, Yaripour et al. (2005) prepared γ-alumina and modified γ-alumina with silica catalysts to be used for methanol dehydration. Almost 100% DME selectivity and approximately 85% methanol conversion were achieved at 300ºC in a fixed bed flow reactor with 0.010 m inner diameter by using 0.5 g catalyst under atmospheric pressure and 11% methanol in nitrogen flow at a rate of 130 cm^3/min. It has been observed that the silica modification has a positive effect on the catalytic activity by increasing the Brønsted acidity in the catalyst. The surface acidity was increased by raising silica loading (3-6 wt%) for the modified catalysts. No by-product formation was observed with this range of silica loadings. On the other hand, it was concluded that an excess amount of silica occupies the active acid sites on the catalyst surface. It has also been reported that dehydration reactions take place mainly on Brønsted acid sites and DME formation occurs especially weak to medium acid sites. Strong acid sites undergo a fairly rapid, irreversible deactivation due to the deposit of heavy secondary products (HCs) inside the pores, called coke. Also, water, the by-product of the dehydration reaction, competes with methanol for the acid sites on alumina. The surface of alumina tended to adsorb water molecules more strongly on the Lewis acid sites. According to the article, the sample with 6 wt% silica loading (DME-AlS3) has exhibited the best methanol conversion.

The same research group (Yaripour et al., 2005) synthesized silica-titania and modified γ-alumina with phosphorus catalysts by sol-gel method to investigate their activities in methanol dehydration. Catalytic activity tests have occurred in the fixed-bed reactor at 300°C under atmospheric pressure and 11% methanol in a nitrogen flow at a rate of 130 cm^3/min (GHSV=15600 h^{-1}) as a feed by using 0.5 g catalyst in the reactor with 0.010 m inner diameter. According to the results obtained, it was shown that the silica-titania catalyst provided a low activity to methanol dehydration due to the low concentration of the acid sites. In contrast, phosphorus-modified γ-alumina catalysts showed the best activity at weak to medium acid sites. Besides the main dimethyl ether, the formation of methane as a by-product was attributed to strong acidic sites, while moderate acidity was claimed to be the key factor to achieve high DME selectivity.

Keshavarz et al. (2010) synthesized γ-Al_2O_3 with a high surface area by using a cationic surfactant, hexadecyl trimethyl ammonium bromide (CTAB), as a template through a simple sol-gel method to enhance the catalytic performance. Tests have occurred in the fixed-bed reactor at 300°C under atmospheric pressure and pure methanol stream (WHSV=1.75-9.62 h^{-1}) by using 1 g catalyst in the reactor with 0.0127 m inner diameter. The produced catalyst was an Al-N prepared with a cationic surfactant. Al-C was a commercial γ-alumina. The addition of surfactant formed micellar structures, prevented the agglomeration of particles during preparation as expected, resulted in a reduction in particle size. The surfactant usage increased the surface area and mesoporosity of the catalyst, Also, it increased the concentration of weak to medium strength acid sites while limiting the number of strong acid sites by reducing the size of crystallization. It was concluded that the smaller crystallite size has more suitable acid sites for methanol dehydration as their accessibility is increased. As a result, good performance was obtained at 300°C and atmospheric pressure. Also, the prepared catalysts remained stable under various weight hourly space velocities (WHSV). It is stated that the selectivity of DME is almost 100% under these reaction conditions.

Tavan et al. (2013) made a comparison between γ-alumina and H-ZSM-5 zeolite performance for methanol dehydration. Catalytic performance tests have occurred in the fixed-bed reactor with 3 g catalyst in 0.019 m inner diameter at 150-400°C under atmospheric pressure and pure methanol stream. It has been found that H-ZSM-5 has higher acidity than γ-alumina and this type of zeolite has better activity compared to the γ-alumina in terms of conversion. However, more activity can cause rapid reactivity when the temperature reaches 400ºC. In the early stages of the reactor, it was observed that low methanol conversion was followed by a low reaction rate at lower temperatures. By increasing temperature, conversion increases and reaches its maximum. Since methanol dehydration is an exothermic reversible reaction, the maximum conversion that can be achieved decreases as the temperature increases. As a result, it was obtained that the limited methanol conversion was about 80% at 250ºC over H-ZSM-5 while 300ºC over γ-alumina catalyst.

As a solution to the rapid reactivity of zeolites, Hassanpour et al. (2010) investigated H-Y and H-ZSM-5 zeolites with various SiO_2/Al_2O_3 ratios to obtain proper acidity for methanol dehydration to DME. Activity tests were taken place in a fixed-bed reactor with 1 g catalyst in 0.0092 m inner diameter under the unchanging operating conditions (T=300ºC, P=16 barg, WHSV=3.8 h^{-1}) and pure methanol stream at a flow rate of 0.55 cm^3/min. The effect of Na content, which reduces the acidity of the catalyst on the catalytic activity, was studied to find out the optimum acidity needed for the process. They reported that all the H-form zeolite catalysts were active and selective for methanol dehydration to DME. It was prepared a series of Na_x-MDHC-1 catalysts where “x” is defined as 100*Na/Al (mol/mol) and varies from 0 to 120 mol% in this work. Among the prepared catalysts, Na_{100}MDHC-1 is the ideal choice as a dehydration catalyst, because it shows the optimum performance in methanol dehydration. The Na-modified catalysts are caused to the significant reduction in the nature of the strong acid sites. Accordingly, increased Na loading makes the catalyst more resistant to hydrocarbon formation.

Tokay et al. (2012) studied methanol dehydration on Al impregnated SBA-15 (i.e., mesoporous structure aluminosilicate). Catalytic performance tests were conducted in a temperature range of 120-450°C under atmospheric pressure and methanol & He feed at a flow rate of 44.4 cm^3/min. According to the results, Al impregnation provided high Brønsted acidity to the catalyst while reducing the pore volume and surface area of SBA-15. This catalyst showed methanol conversion of about 80% and nearly 100% DME selectivity, at temperatures over 300ºC. The commercial alumina catalyst, which they made the comparison, was also showed very good performance for methanol dehydration at temperatures lower than 300ºC.

Dai et al. (2011) worked on the synthesis of a series of aluminophosphate and silicoaluminophosphate molecular sieves, i.e., AlPO-5, AlPO-11, AlPO-41, SAPO-5, SAPO-11, SAPO-41, and tested their performances in the temperature range of 250-400°C by using 0.4 g catalyst on the methanol dehydration reaction. The methanol dehydration reaction was carried out in a fixed-bed flow microreactor under atmospheric pressure and 0.008 cm^3/min pure methanol feed flow. SAPO-11, having weak acid sites together with moderate acid sites in low concentration, showed high activity for DME synthesis at 250°C. By using SAPO-11 at 250°C, methanol conversion over 85% with

DME selectivity higher than 99.9% could be attained for 200 hours. As the temperature was increased to 300-400°C, moderate acid sites in silico-aluminophosphates caused side reactions to proceed, and the yield of DME decreased. On the other hand, by using AlPO-5, AlPO-11, and AlPO-41 catalysts, DME became the primary product in the temperature range of 250-400°C. For AlPO-5, AlPO-11, and AlPO-41, the maximum DME yield which was slightly higher than 80%, was obtained at 350°C. It was found that these three catalysts possess good durability for methanol dehydration at 350°C.

The Al-HMS (i.e., Al incorporated hexagonal mesoporous silica) with different Si/Al ratios has been synthesized by Sabour et al. (2014) and tested for DME production by methanol dehydration reaction in the temperature range of 250-400°C by using 0.5 g catalyst and 11% methanol in nitrogen as a feed. According to the article, pure mesoporous silica does not have enough acidity for the reaction, but acidity can be increased by introducing foreign metal ions such as Al during the synthesis. They reported that moderate acid strength is favorable for methanol dehydration reaction. Al-HMS with a Si/Al ratio of 10 which had moderate acidity showed the best catalytic activity with methanol conversion of 89% with 100% DME selectivity. With increasing acidity when the Si/Al ratio was decreased, the conversion increased but DME selectivity decreased due to by-product formation.

All in all, when the literature is reviewed, it is seen that the acidic properties of catalysts with weak to medium acid sites required for methanol dehydration are modified in various ways. It has been observed that some comparisons have not been made in the literature. In this study, besides changing the parameters such as catalyst composition, calcination temperature, catalyst peptizer for testing in methanol dehydration, the activities were compared by adding ZSM-5 to SiO_2/Al_2O_3 catalysts to observe the effect of acidity and acidic strength on the activity.

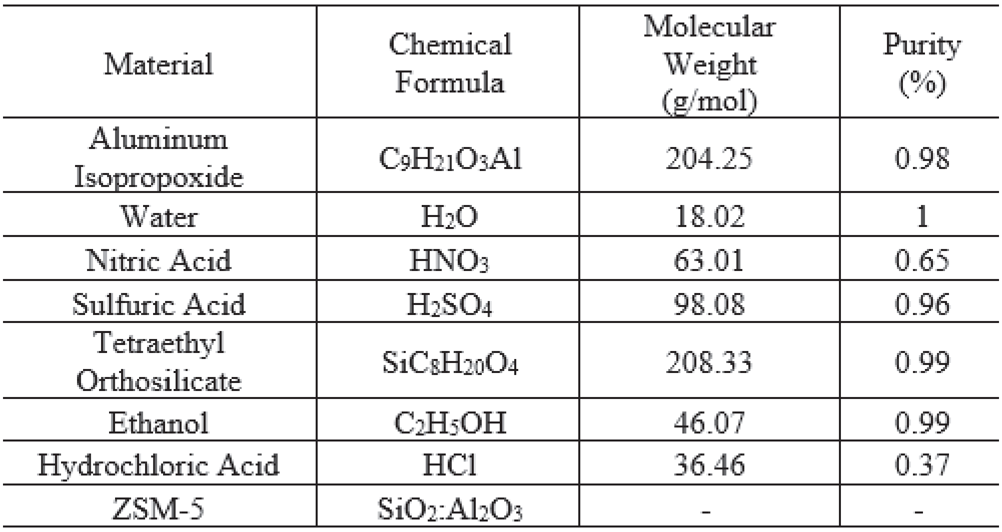
CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Silica-alumina (SiO_2/Al_2O_3) catalysts with different compositions which are 25/75 wt.%, 50/50 wt.%, 75/25 wt.% were synthesized by the sol-gel method for the methanol dehydration reaction. Aluminum isopropoxide (AIP, Sigma-Aldrich) was used as a precursor, deionized water (DIW) was used as a solvent, and nitric acid (HNO_3, VWR Chemicals) was used as a peptizer in the alumina synthesis. For silica, tetraethyl orthosilicate (TEOS, Fluka) was used as a precursor, ethanol (EtOH, Sigma-Aldrich), and deionized water (DIW) were used as a solvent, and hydrochloric acid (HCl) was used as a peptizer. Afterward, the peptizer was changed to sulfuric acid (H_2SO_4, Sigma-Aldrich) for alumina, and/or 10wt.% of ZSM-5 (Alfa Aesar) zeolite with 200:400/1 silica-alumina ratio (about 90% silica content) was added in some silica-alumina catalysts. The information of the chemicals used in the silica-alumina synthesis by the sol-gel method is given in Table 3.1.

Table 3.1. List of properties of chemicals used in the synthesis of catalysts



Material	Chemical Formula	Molecular Weight (g/mol)	Purity (%)
Aluminum Isopropoxide	$C_9H_{21}O_3Al$	204.25	0.98
Water	H_2O	18.02	1
Nitric Acid	HNO_3	63.01	0.65
Sulfuric Acid	H_2SO_4	98.08	0.96
Tetraethyl Orthosilicate	$SiC_8H_{20}O_4$	208.33	0.99
Ethanol	C_2H_5OH	46.07	0.99
Hydrochloric Acid	HCl	36.46	0.37
ZSM-5	$SiO_2:Al_2O_3$	-	-

3.2. Methods

The experimental part of this study is divided into 4 sections which are catalyst preparation by sol-gel method, catalyst characterization by using NH_3-TPD, the testing setup to determine the catalytic performance of catalysts, and product analysis by using GC-MS at the end of the reaction.

3.2.1. Catalysts Preparation

The sol-gel method was used to prepare SiO_2/Al_2O_3 catalysts in Prof. Dr. Erol Şeker's laboratory.

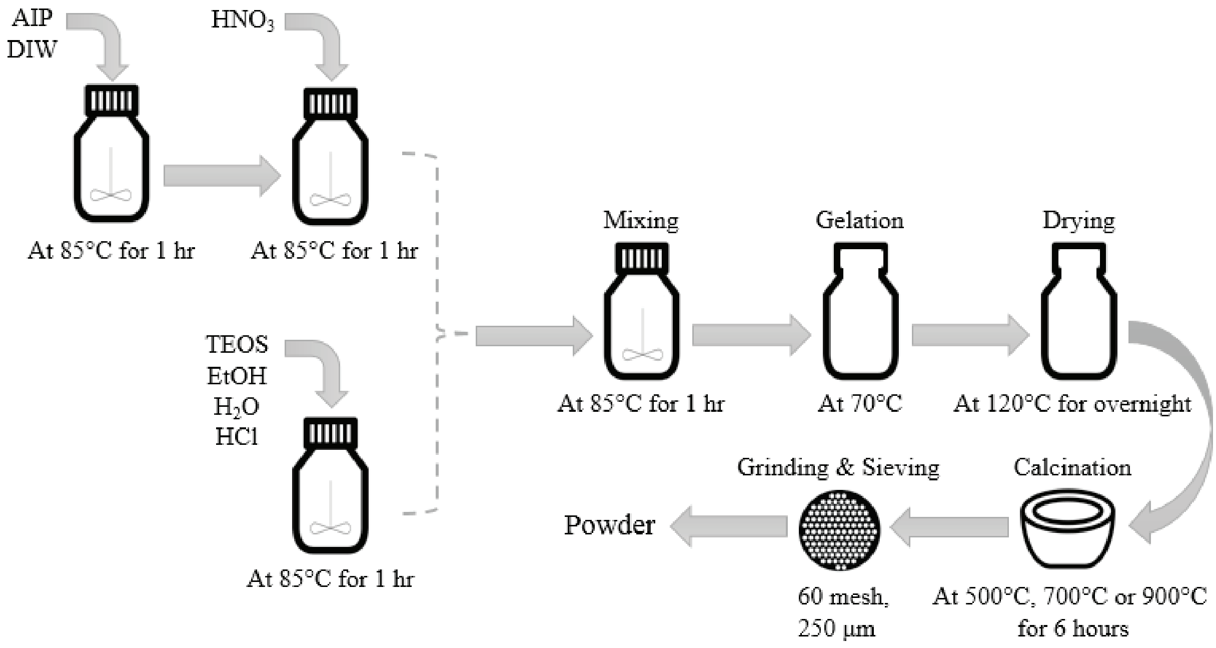


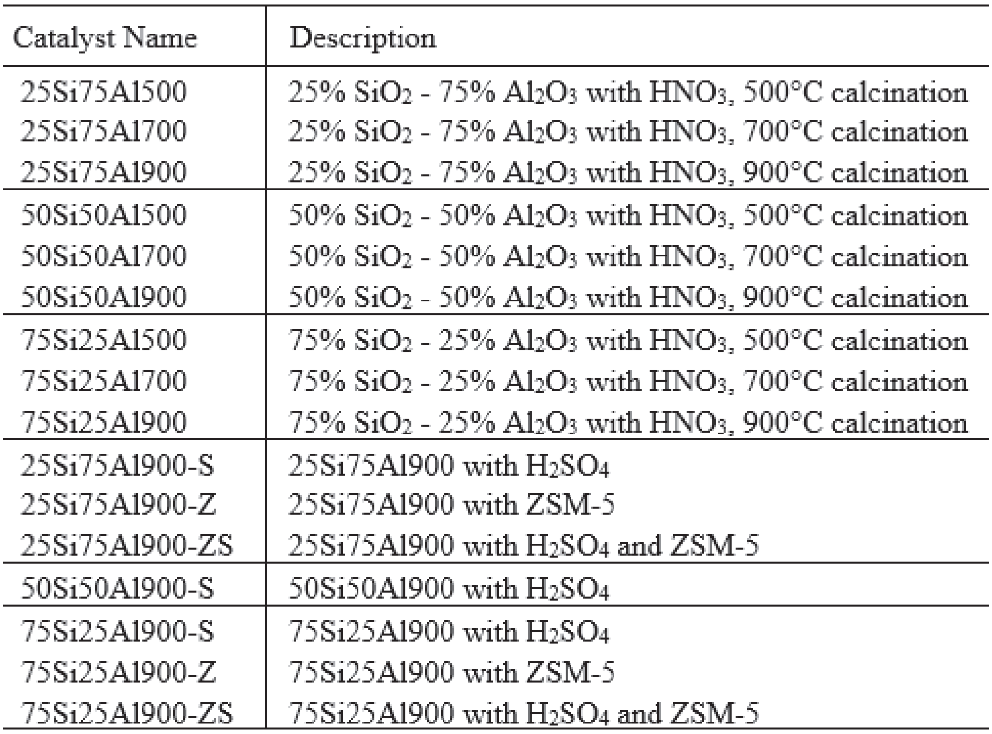
Figure 3.1. The preparation procedure of SiO_2/Al_2O_3 catalysts with HNO_3

For alumina, the alumina precursor aluminum isopropoxide (AIP) and deionized water (DIW) were mixed in required amounts at 85°C under vigorous stirring at 900 rpm for 1 hour in a Schott bottle to be taken place hydrolysis reaction. After 1 hour, HNO_3 was added to the mixture and the mixture was again allowed to stir vigorously for 1 hour at 85°C. Meanwhile, materials for silica were prepared in another Schott bottle. Silica precursor tetraethyl orthosilicate (TEOS), DIW and ethanol (EtOH), and peptizer HCl were put into the bottle at the same time and mixed for 1 hour at 85°C. After 1 hour, the alumina sol and the silica sol were obtained and they were mixed and stirred at 85°C for

1 hour. After the mixing period was over, the mixture was left for gelation at 70°C without any stirring to evaporate the water slowly. At this stage, the condensation polymerization reaction also took place. Then, the mixture that became soft gel was left in the dryer at 120°C for overnight and the solvent was completely evaporated before the calcination. After the drying step, each catalyst was calcined at 500°C, 700°C and 900°C for 6 hours with 10°C/min heating rate in air. Finally, the calcined catalysts were ground and sieved to 60 mesh (250 μm) to eliminate the internal mass transfer limitation and avoid excessive pressure drop during the reaction (Figure 3.1).

In the SiO_2/Al_2O_3 catalysts produced at 3 different compositions (25/75 wt.%, 50/50 wt.%, 75/25 wt.%) and 3 different calcination temperatures (500°C, 700°C, 900°C), some changes were made in the catalyst formulations of the most active and the least active catalysts in terms of catalytic performance to modify acidic properties. In this regard, the formulation of the most active and the least active catalysts was changed as follows: In the alumina preparation stage, the peptizer acid was changed from HNO_3 to H_2SO_4. The remaining procedure has not been changed. To investigate a different catalyst, 0.1 g ZSM-5 zeolite was added to the silica-alumina sol mixture step, and the mixture sol was left to stir vigorously for 1 hour at 85°C. Again, the rest of the procedure was followed the same. All the produced catalysts mentioned throughout the thesis are listed in Table 3.2.

Table 3.2. List of produced SiO_2/Al_2O_3 catalysts and their identifications



Catalyst Name	Description
25Si75Al500	25% SiO_2 - 75% Al_2O_3 with HNO_3, 500°C calcination
25Si75Al700	25% SiO_2 - 75% Al_2O_3 with HNO_3, 700°C calcination
25Si75Al900	25% SiO_2 - 75% Al_2O_3 with HNO_3, 900°C calcination
50Si50Al500	50% SiO_2 - 50% Al_2O_3 with HNO_3, 500°C calcination
50Si50Al700	50% SiO_2 - 50% Al_2O_3 with HNO_3, 700°C calcination
50Si50Al900	50% SiO_2 - 50% Al_2O_3 with HNO_3, 900°C calcination
75Si25Al500	75% SiO_2 - 25% Al_2O_3 with HNO_3, 500°C calcination
75Si25Al700	75% SiO_2 - 25% Al_2O_3 with HNO_3, 700°C calcination
75Si25Al900	75% SiO_2 - 25% Al_2O_3 with HNO_3, 900°C calcination
25Si75Al900-S	25Si75Al900 with H_2SO_4
25Si75Al900-Z	25Si75Al900 with ZSM-5
25Si75Al900-ZS	25Si75Al900 with H_2SO_4 and ZSM-5
50Si50Al900-S	50Si50Al900 with H_2SO_4
75Si25Al900-S	75Si25Al900 with H_2SO_4
75Si25Al900-Z	75Si25Al900 with ZSM-5
75Si25Al900-ZS	75Si25Al900 with H_2SO_4 and ZSM-5

3.2.2. Catalysts Characterization

Methanol dehydration takes place on acidic catalysts. Temperature Programmed Desorption (TPD) as a chemisorption analysis equipped with Micromeritics AutoChem II 2920 was used to determine the total amount of acid sites (i.e., acidity) and acidic strength of the catalysts by using ammonia (NH_3) as a probe base molecule. The amount of NH_3 desorbed from the active sites on the catalyst surface is the determining criterion for acidity and the maximum desorption temperature is for acidic strength. Initially, the catalysts are activated by heating up to 500ºC with a heating rate of 15ºC/min for 30 minutes. Then, the system is cooled to 55ºC. At this temperature, adsorption is carried out on approximately 100 mg of fresh catalyst at a flow rate of 30 cm^3/min of NH_3-He flow for 1 hour. Afterward, desorption takes place under He gas flow at a rate of 70 cm^3/min with temperature increasing up to 500ºC for 1 hour. When the bonds between the adsorbent and the adsorbate are broken, the desorbed molecules enter the He stream and are swept into the detector which measures the gas concentration by using thermal conductivity. The acidity and acidic strength values of the catalysts are reached by processing data which are the signals coming out of the detector, time and temperature values.

3.2.3. Catalytic Performance Tests

The SiO_2/Al_2O_3 catalysts produced for methanol dehydration were tested in a fixed bed quartz reactor with a 4 mm inner diameter. The reaction equipment setup is shown in Figure 3.2. Before the reaction step, equilibrium conversion of methanol was calculated and it was found to be 99% to know the thermodynamic boundaries of the reaction.

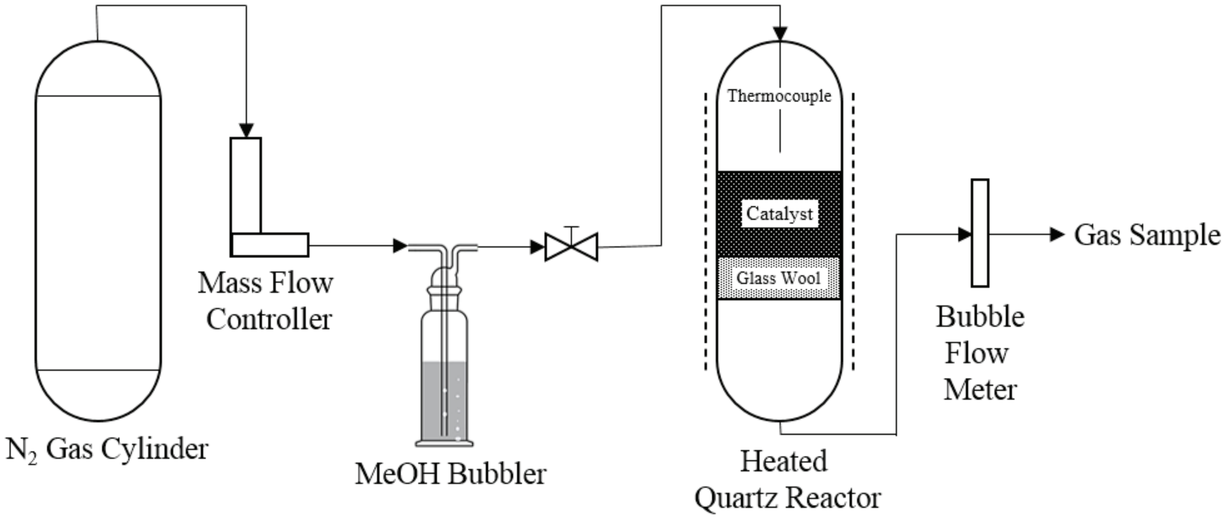


Figure 3.2. The experimental setup for methanol dehydration to dimethyl ether

On the reactor side in Figure 3.2, approximately 100 mg of catalyst, supported by glass wool, was placed inside the quartz reactor at a height of 1 cm by considering residence time. While the furnace surrounding the reactor was heated to the required reaction temperature, a pure nitrogen flow was passed through the reactor at a rate of 100 cm^3/min. The required reaction temperature was initially set at 400°C and then 300°C at atmospheric pressure. When the temperature value measured from the thermocouple reached the desired reaction temperature, the methanol was put into the gas bubbler and the nitrogen was flowed to one side of the bubbler to evaporate the methanol at a volumetric flow rate of 100 cm^3/min to eliminate external mass transfer limitation. Thus, the nitrogen & methanol gas mixture was fed to the system and the reaction started. The methanol dehydration reaction took place at 400°C and then at 300°C for both 30 minutes. During the reaction, the volumetric flow rate, which was approximately 105 cm^3/min, was read from the bubble flow meter every 2 minutes. This value indicated that there is about 5% amount of methanol going through the reactor. Finally, the gas mixture leaving the reactor was analyzed in GC-MS, when the reaction was ensured to reach a steady-state in 30 minutes was finished. The methanol dehydration reaction, which was performed once for each catalyst, was tested 5 more times for the catalyst with the best activity. Thus, standard deviation (σ), uncertainty (δ), and error, which is 5.5%, calculations in 95% confidence interval were made with the conversion values obtained through GC-MS analysis by following equations:

$$\delta = \frac{\sigma \times t_{N-1}}{\sqrt{N}}, \quad \text{Error\%} = \frac{\delta}{\text{Mean}} \times 100 \qquad \text{(Eq. 3)}$$

3.2.4. Product Analysis

The reaction product was analyzed by GC-MS technique (gas chromatography-mass spectroscopy) in Agilent 6890N Network Gas Chromatograph equipped with a capillary HP-5MS column, qualitatively. The methanol conversion values with 5.5% error were calculated based on the chromatograms obtained from the analysis by the following equation:

$$\mathrm{X_{MEOH}} = \frac{\mathrm{F_{MEOH,in}} - \mathrm{F_{MEOH,out}}}{\mathrm{F_{MEOH,in}}} \pm \delta \qquad \text{(Eq. 4)}$$

CHAPTER 4

RESULTS AND DISCUSSION

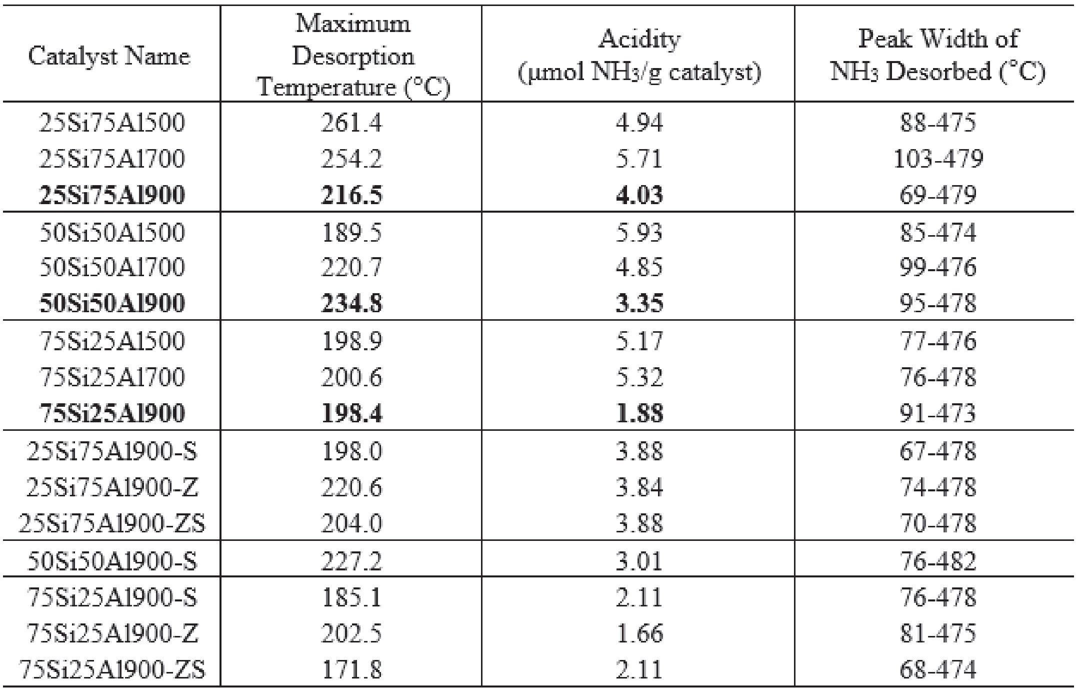
4.1. Characterization Results

The NH_3-TPD analysis was used to understand the acidic properties of all synthesized SiO_2/Al_2O_3 catalysts to be used for methanol dehydration to DME reaction.

4.1.1. Temperature Programmed Desorption (NH_3-TPD) Results

According to the NH_3-TPD analysis, the maximum desorption temperature values at which NH_3 is adsorbed from the catalysts give the acidic strength, while the total amount of acid sites gives the total acidity information. These values are shown in Table 4.1. The catalysts on which modifications were made later are shown in bold in Table 4.1. The graphs of Signal vs. Time and Temperature vs. Time, obtained by NH_3-TPD analysis of all catalysts, are available in Appendix A.

Table 4.1. Acidic properties of the all synthesized SiO_2/Al_2O_3 catalysts



Catalyst Name	Maximum Desorption Temperature (°C)	Acidity (μmol NH_3/g catalyst)	Peak Width of NH_3 Desorbed (°C)
25Si75Al500	261.4	4.94	88-475
25Si75Al700	254.2	5.71	103-479
25Si75Al900	**216.5**	**4.03**	69-479
50Si50Al500	189.5	5.93	85-474
50Si50Al700	220.7	4.85	99-476
50Si50Al900	**234.8**	**3.35**	95-478
75Si25Al500	198.9	5.17	77-476
75Si25Al700	200.6	5.32	76-478
75Si25Al900	**198.4**	**1.88**	91-473
25Si75Al900-S	198.0	3.88	67-478
25Si75Al900-Z	220.6	3.84	74-478
25Si75Al900-ZS	204.0	3.88	70-478
50Si50Al900-S	227.2	3.01	76-482
75Si25Al900-S	185.1	2.11	76-478
75Si25Al900-Z	202.5	1.66	81-475
75Si25Al900-ZS	171.8	2.11	68-474

As can be seen from the maximum desorption temperature values in Table 4.1, all catalysts have weak strength acid sites (i.e., maximum desorption temperature between 100°C-350°C). Considering the calcination temperatures of the catalysts, a decrease in the acidity of the catalysts calcined at 900°C is observed. There is not much difference and no correlation between the effect of other calcination temperatures (i.e., 500°C, 700°C) in 25/75, 50/50, and 75/25 SiO_2/Al_2O_3 groups. The catalyst with the lowest acidity value is 75Si25Al900. The most successful catalyst group in terms of both acidity and acidic strength is the 25/75 SiO_2/Al_2O_3 group. According to the activity analysis, when the catalysts produced later were examined, it was observed that the acidity of the catalysts with ZSM-5 decreased, but the acidic strength slightly increased with zeolite addition. Likewise, the acidity was reduced by changing the content of the catalyst from nitric acid to sulfuric acid. However, the acidity of the 75Si25Al900 catalyst, which has the lowest acidity, increased with sulfuric acid. Apart from that, the acidity of the catalysts, which are only subjected to sulfuric acid exchange, and to which both sulfuric acid and ZSM-5 exchange are applied, are the same. Also, sulfuric acid and/or zeolite treatment to the 25Si75Al900 catalyst did not change the acidity much. In the statistical error calculation, the error of the NH_3-TPD analysis was 15% with 3 reps for calibration factor calculation, thus the influence of acidity on the catalyst activity may vary during the reaction. However, it was observed that some acidity-activity correlations were still obtained with the activity results to be explained later.

4.2. Activity Results

Methanol conversions and product analysis for all catalysts were obtained by GC-MS chromatograms. For the activity comparison, catalysts were synthesized in different compositions and calcination temperatures at first, and then the catalyst content was changed in some catalysts. The methanol dehydration reaction was carried out at 300°C and 400°C.

4.2.1. Effect of Compositions and Calcination Temperatures

In order to test the effect of the catalyst composition on the activity, SiO_2/Al_2O_3 catalysts were synthesized by sol-gel method in 3 compositions as 25/75, 50/50, and 75/25 wt% and for the effect of calcination temperature on the activity, the catalysts were calcined at 500°C, 700°C, and 900°C.

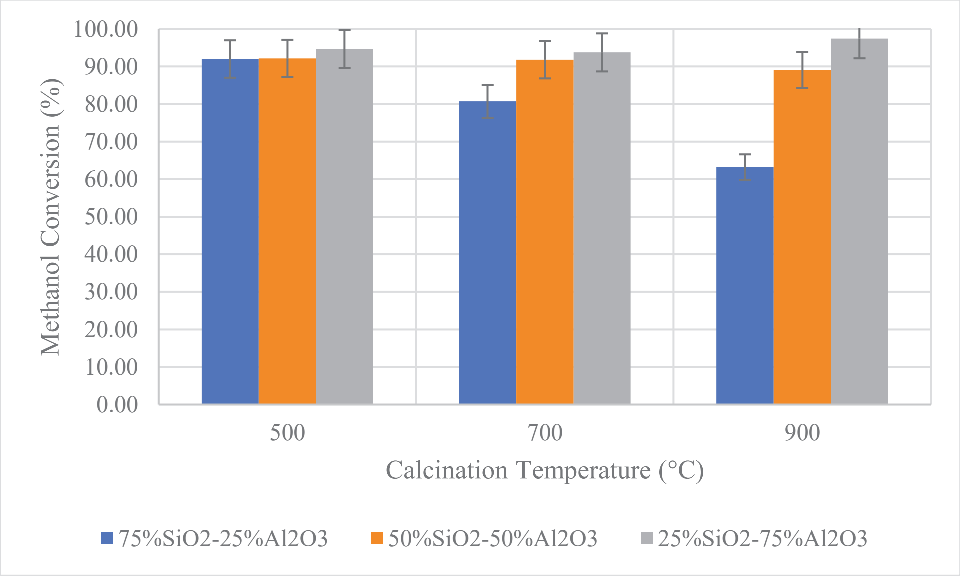


Figure 4.1. The activity of catalysts of different calcination temperatures and compositions in the methanol dehydration to DME reaction

The value of the error bar seen in Figure 4.1 was calculated as 5.5%. As can be seen, although SiO_2/Al_2O_3 catalysts with 25/75 and 50/50 compositions were calcined at 3 different calcination temperatures, their activities did not change much. However, the activity of SiO_2/Al_2O_3 catalyst with 75/25 composition decreases significantly as the calcination temperature increases. The activities of all catalysts calcined at 500°C are close to each other, whereas there is a big difference in activity between 25/75 and 75/25 catalysts calcined at 900°C. As evidence of the NH_3-TPD results, 25/75 catalyst calcined at 900°C (i.e., 25Si75Al900) was the most active catalyst with approximately 97% methanol conversion, while 75/25 catalyst calcined at 900°C (i.e., 75Si25Al900) was the least active catalyst with 63% conversion. The 50/50 catalyst (50Si50Al900) calcined at 900°C, which is statistically tied with 25Si75Al900, is also a very active catalyst with over 90% conversion. The later treatments to modify the acidic properties of the catalysts were tested on these 3 catalysts (i.e., 25Si75Al900, 50Si50Al900, 75Si25Al900). In addition, the DME selectivity for all catalysts is approximately 100%.

4.2.2. Effect of Catalyst Ingredients and Reaction Temperatures

To examine the effect of the peptizer contained in the catalyst, the content of 25Si75Al900, 50Si50Al900, and 75Si25Al900 catalysts was changed from nitric acid to sulfuric acid. Differently, the ZSM-5 zeolite was added to 25Si75Al900 and 75Si25Al900 catalysts containing nitric acid or sulfuric acid, and the activity of the catalysts in the methanol dehydration to DME reaction was investigated.

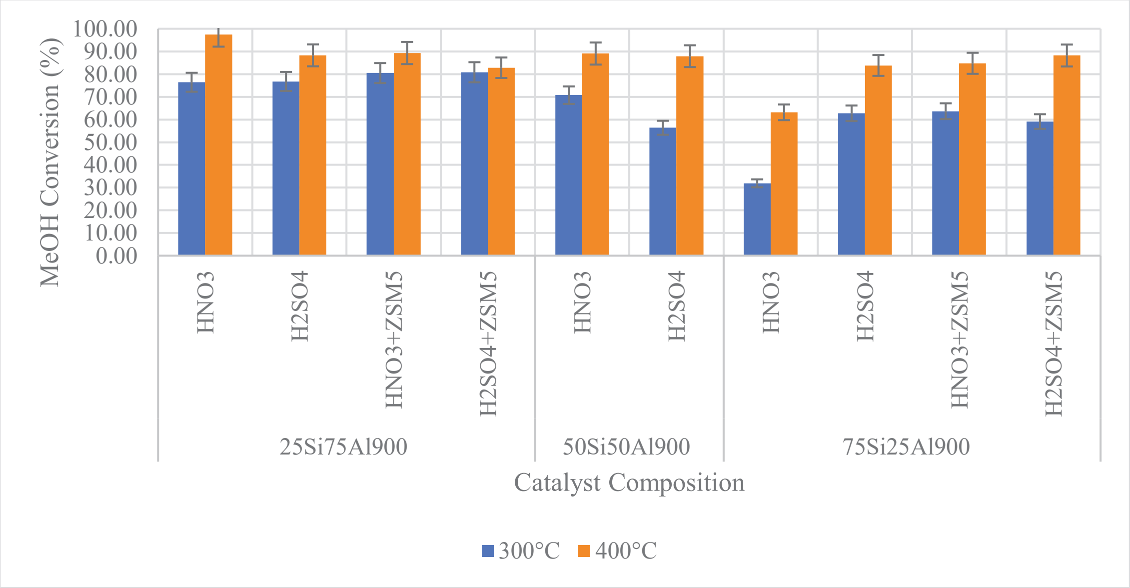


Figure 4.2. The activity of catalysts with different contents at different reaction temperatures in the methanol dehydration to DME reaction

According to Figure 4.2, at 400°C methanol dehydration to DME reaction, the most significant change was observed in the 75Si25Al900 catalyst, considering the 5.5% error. The 75Si25Al900 catalyst, which gave 63% conversion with nitric acid, increased the conversion value to about 85% with sulfuric acid as a catalyst name of 75Si25Al900-S. The addition of zeolite to this catalyst (i.e., 75Si25Al900-Z, 75Si25Al900-ZS) did not change much of its activity obtained in its value with sulfuric acid. When the reaction temperature was 300°C, the conversion of 75Si25Al900-S, 75Si25Al900-Z, 75Si25Al900-ZS catalysts decreased from about 85% to 60%. The 75Si25Al900 catalyst with nitric acid still showed the least activity as at 400°C and gave about 30% conversion at 300°C.

For the 25Si75Al900 catalyst, which is the most active catalyst has 97% conversion, sulfuric acid and/or zeolite change did not add a great change to the activity at 400°C. This correlation is also seen in the NH_3-TPD results. When the reaction temperature is 300°C, the 25Si75Al900 and 25Si75Al900-S catalysts experienced a slight decrease in terms of methanol conversion, while the conversion drop at 25Si75Al900-Z and 25Si75Al900-ZS catalysts with zeolite from about 85% to 80% are within the error bar limits. It can be seen that the best performing catalysts at the reaction temperature of 300°C are in 25/75 wt.% composition.

The 50Si50Al900 and 50Si50Al900-S catalysts showed similar activities at the reaction temperature of 400°C with about 90% conversion. When the reaction temperature was 300°C, the conversion of the 50Si50Al900 catalyst decreased to about 70%, while the conversion of the 50Si50Al900-S catalyst decreased to about 55%. Here, the performance of the catalyst with nitric acid is higher than the catalyst with sulfuric acid at 300°C. As mentioned before in NH_3-TPD results, the sulfuric acid modification made weaker acidity of the catalysts. The effect of this situation is seen as an activity in the composition of 50/50 wt.% at 300°C reaction temperature.

As a result, all synthesized SiO_2/Al_2O_3 catalysts are active and selective for methanol dehydration to DME reaction. The performance of all catalysts at 400°C is higher than at 300°C reaction temperature. The most active catalyst is 25Si75Al900 while the least active catalyst is 75Si25Al900 at both reaction temperatures. While sulfuric acid and/or zeolite exchange increased the performance of the least active catalyst, it did not reveal much difference in the most active catalysts. The DME selectivity for all catalysts is approximately 100%.

CHAPTER 5

CONCLUSION

In this study, it was investigated that the acidic strength, acidity, and activity of the silica-alumina catalysts which were used for DME production by a methanol dehydration reaction. For this purpose, SiO_2/Al_2O_3 acidic catalysts with different compositions as 25/75 wt.%, 50/50 wt.%, 75/25 wt.% and different calcination temperatures which are 500°C, 700°C and 900°C were produced by sol-gel method. According to the catalytic performance of silica-alumina catalysts, the contents of the most active and the least active ones were then updated with the addition of H_2SO_4 and/or ZSM-5 zeolite, then acidic properties and activities were investigated. The acidic properties of the catalysts were determined by NH_3-TPD analysis, while the GC-MS technique was used for product analysis.

During the reaction, approximately 100 mg of silica-alumina catalyst at a height of 1 cm was present in the reactor. The nitrogen and methanol mixture fed to the reactor at the volumetric flow rate of 100 cm^3/min via gas bubbler. The methanol dehydration reaction took place at 400°C and then at 300°C for both 30 minutes.

Results have shown that there was a decrease in the acidity of the catalysts calcined at 900°C. The activity of the 75Si25Al900 catalyst decreases significantly as the calcination temperature increases. The activities of all catalysts calcined at 500°C are close to each other, whereas there is a big difference in activity between 25%SiO_2-75%Al_2O_3 and 75%SiO_2-25%Al_2O_3 catalysts calcined at 900°C. The performance of all catalysts at 400°C is higher than at 300°C reaction temperature. The 25/75 wt.% SiO_2/Al_2O_3 catalysts were performed well at both 300°C and 400°C reaction temperatures. As evidence of the NH_3-TPD results, 25Si75Al900 was the most active catalyst with approximately 97% methanol conversion at 400°C reaction temperature, while 75Si25Al900 was the least active catalyst with 63% conversion at 400°C. The 50Si50Al900 is also a very active catalyst with over 90% conversion at 400°C. Sulfuric acid and/or zeolite exchange increased the performance of the least active catalyst, while it did not reveal much difference in the most active catalysts. The addition of ZSM-5 zeolite slightly increased the acidic strength of the catalysts. The margin of error of the experiments was calculated as 5.5% with 6 reps at the 95% confidence interval.

This study includes some limitations that are included in the margin of error as 5.5%. For these, undesirable hard gelation formations during the synthesis of silica-alumina by sol-gel method, the fact that the air temperature is not always the same during the synthesis and reaction process, and limitations that vary according to the equipment in which the analyzes are made and the specialist who performs the analysis can be shown.

As a result, the effect of the acidic properties of the catalysts on the activity was investigated for the methanol dehydration reaction by making some modifications on the acidic silica-alumina catalysts. It is seen that all catalysts have weak acid properties and they are active and selective for dimethyl ether (DME) production from methanol.

For further suggestions, it may be recommended to try longer reaction times, more repeat reactions with the catalysts, and different reaction temperatures to examine the state of the catalyst performance and the product distributions.

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APPENDIX

NH_3-TPD PROFILES OF ALL CATALYSTS

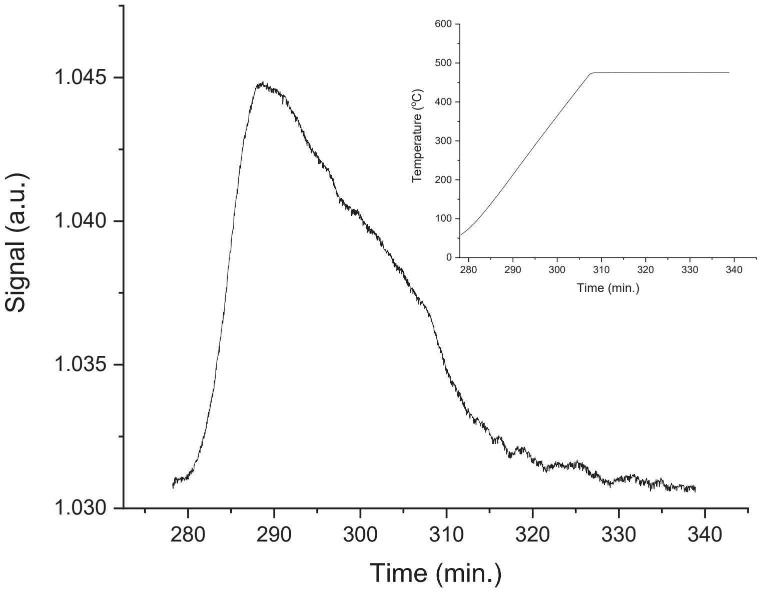

Figure A.1. The NH_3-TPD profile of 75Si25Al500 catalyst

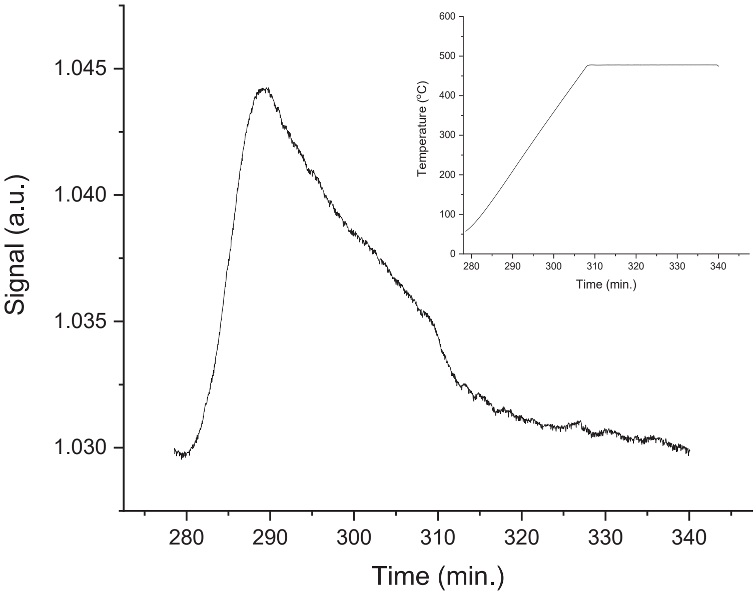

Figure A.2. The NH_3-TPD profile of 75Si25Al700 catalyst

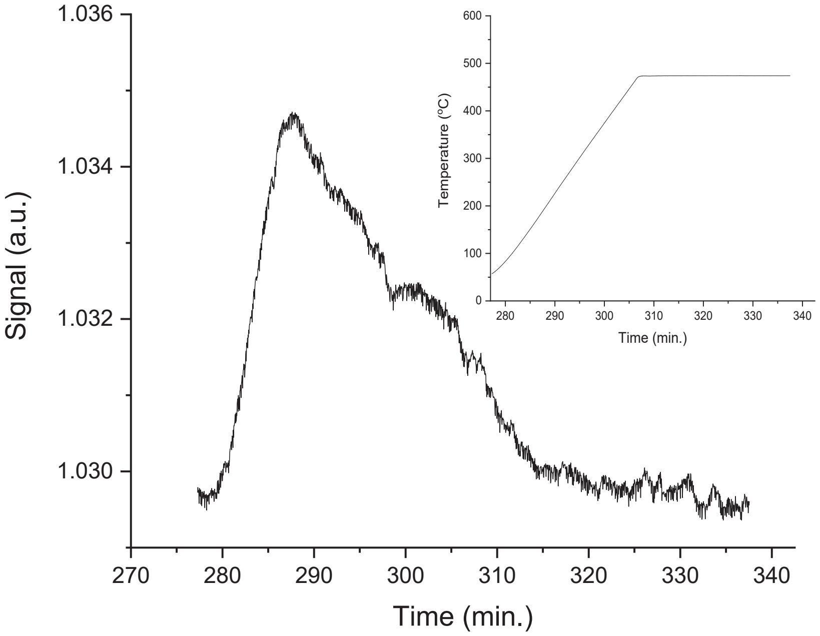

Figure A.3. The NH_3-TPD profile of 75Si25Al900 catalyst

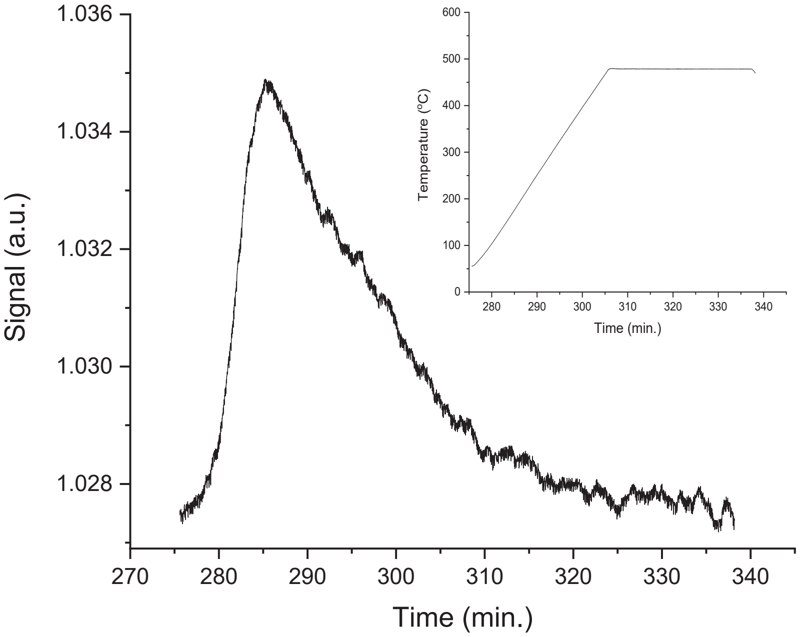

Figure A.4. The NH_3-TPD profile of 75Si25Al900-S catalyst

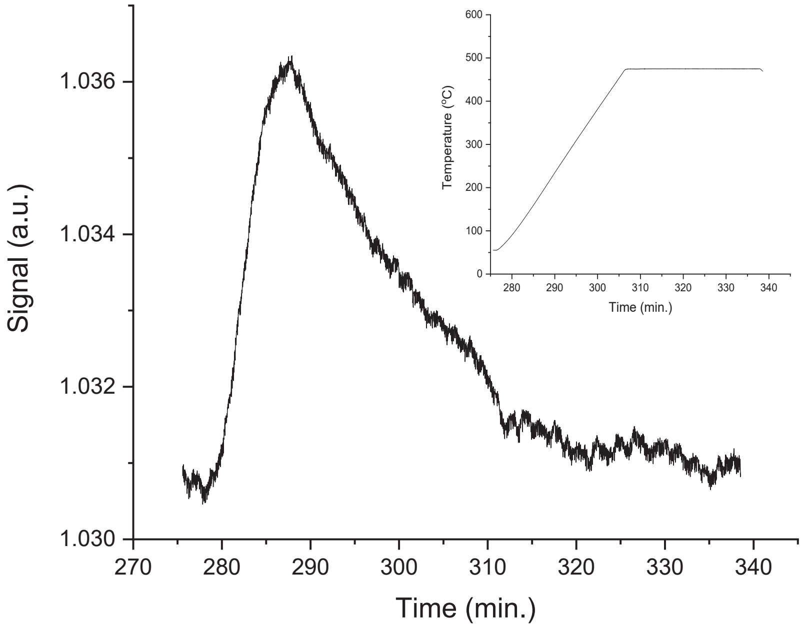

Figure A.5. The NH$_3$-TPD profile of 75Si25Al900-Z catalyst

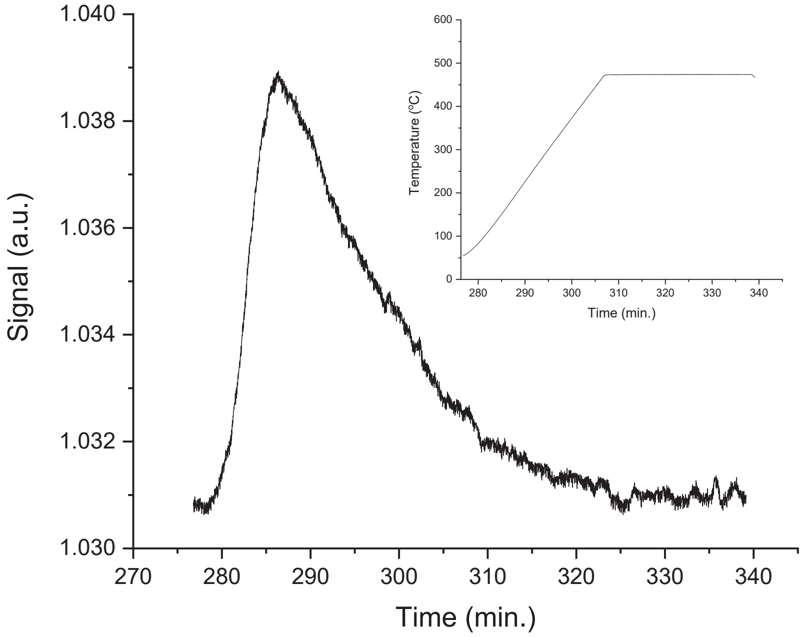

Figure A.6. The NH$_3$-TPD profile of 75Si25Al900-ZS catalyst

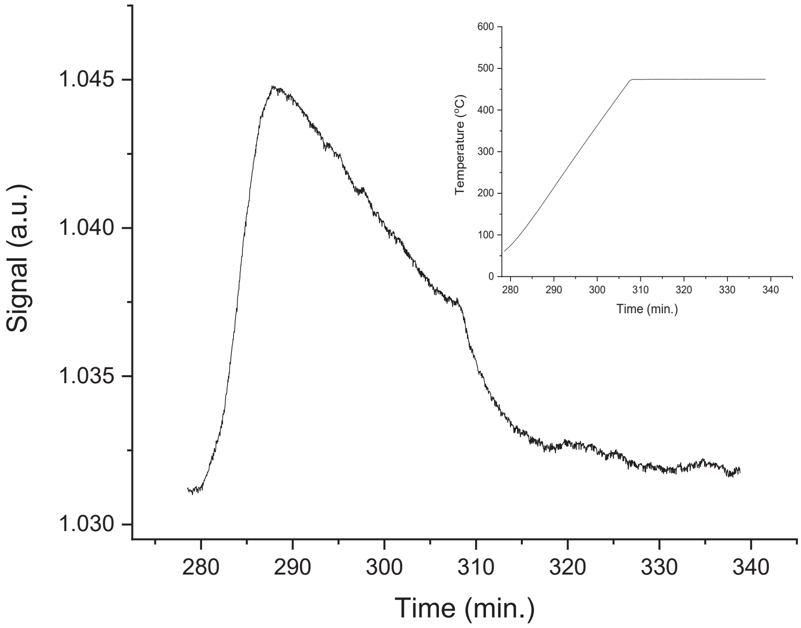

Figure A.7. The NH_3-TPD profile of 50Si50Al500 catalyst

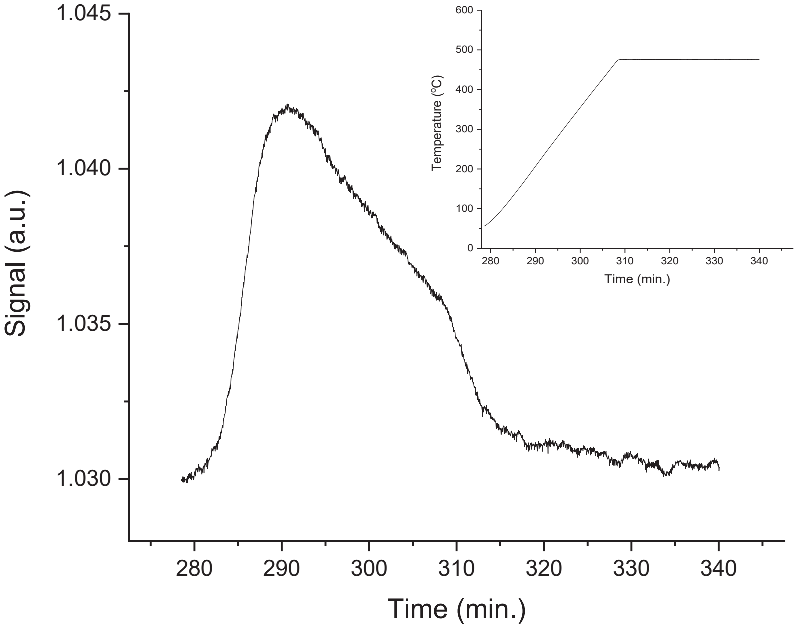

Figure A.8. The NH_3-TPD profile of 50Si50Al700 catalyst

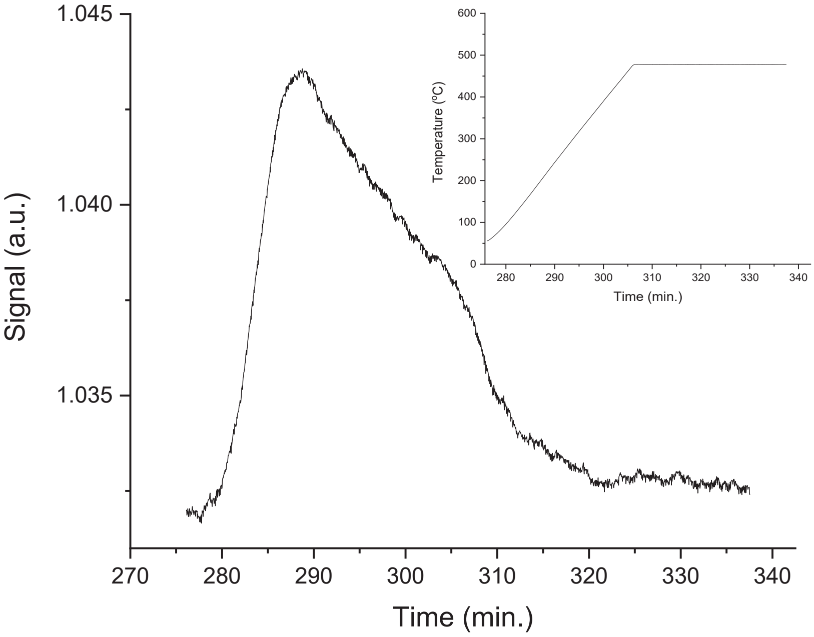

Figure A.9. The NH_3-TPD profile of 50Si50Al900 catalyst

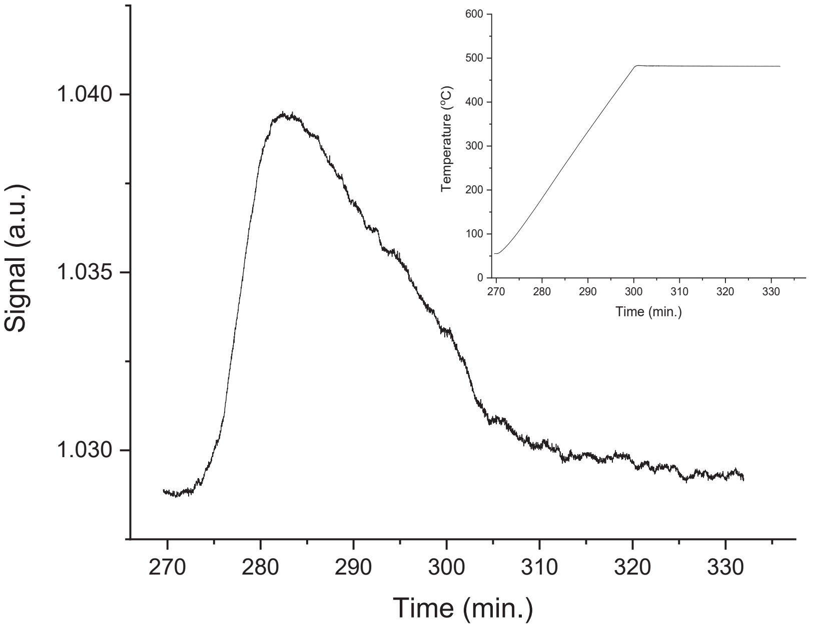

Figure A.10. The NH_3-TPD profile of 50Si50Al900-S catalyst

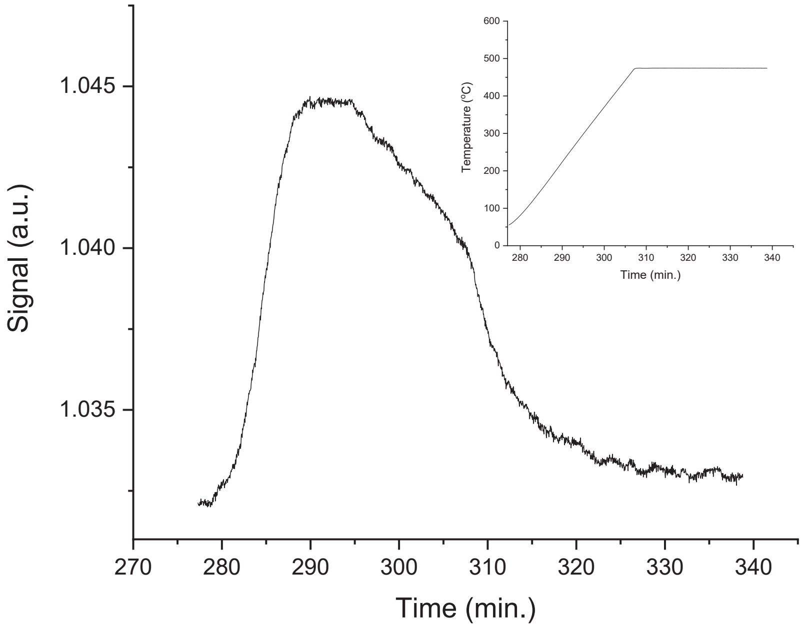

Figure A.11. The NH_3-TPD profile of 25Si75Al500 catalyst

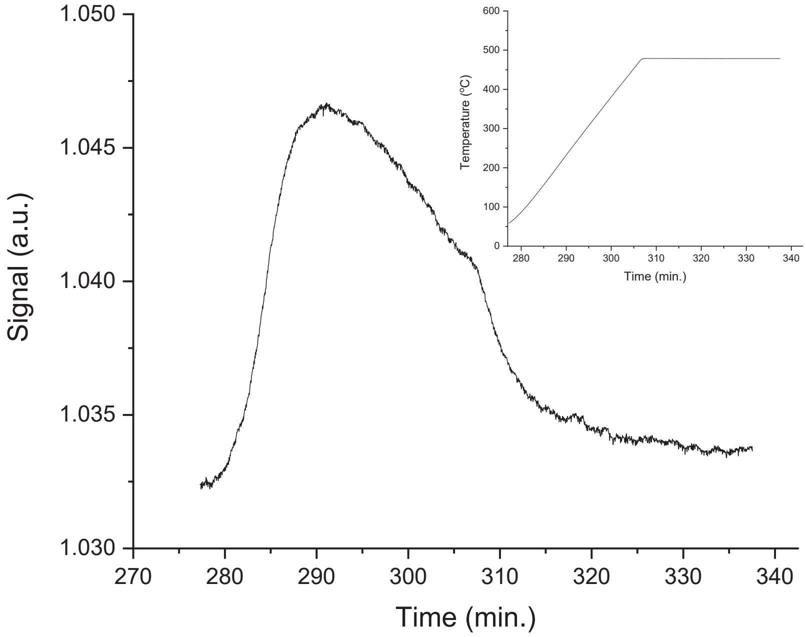

Figure A.12. The NH_3-TPD profile of 25Si75Al700 catalyst

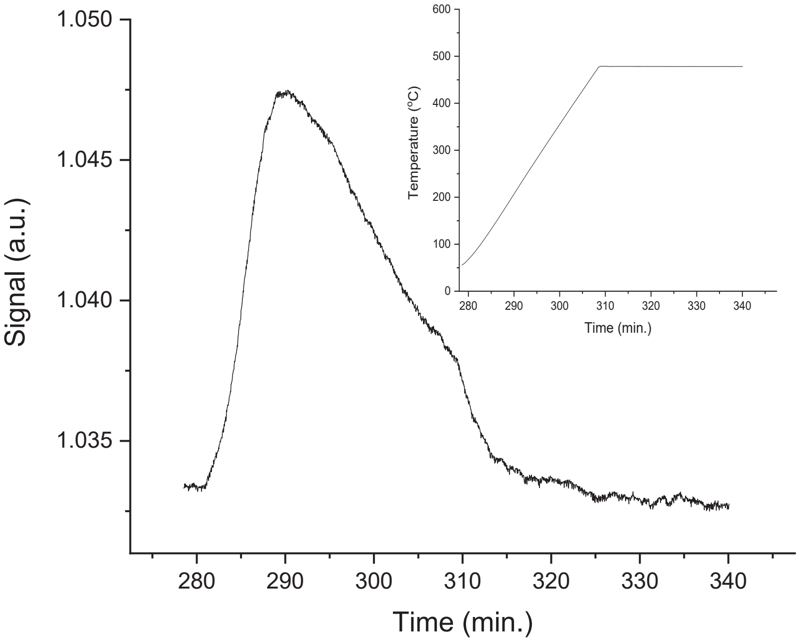

Figure A.13. The NH_3-TPD profile of 25Si75Al900 catalyst

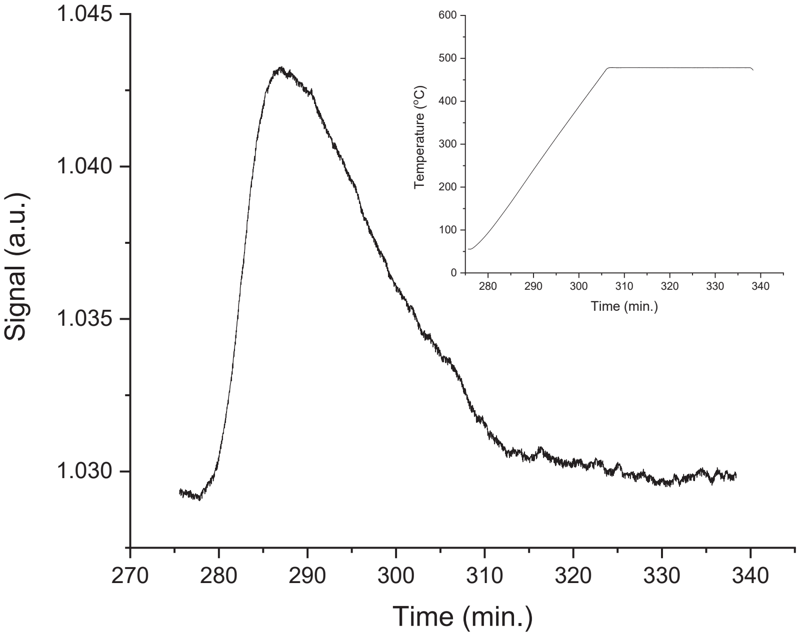

Figure A.14. The NH_3-TPD profile of 25Si75Al900-S catalyst

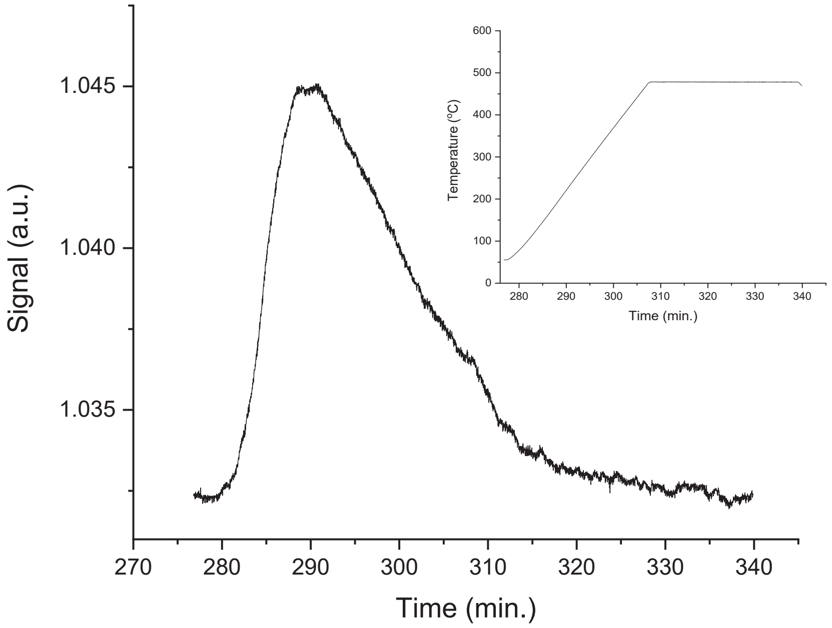

Figure A.15. The NH_3-TPD profile of 25Si75Al900-Z catalyst

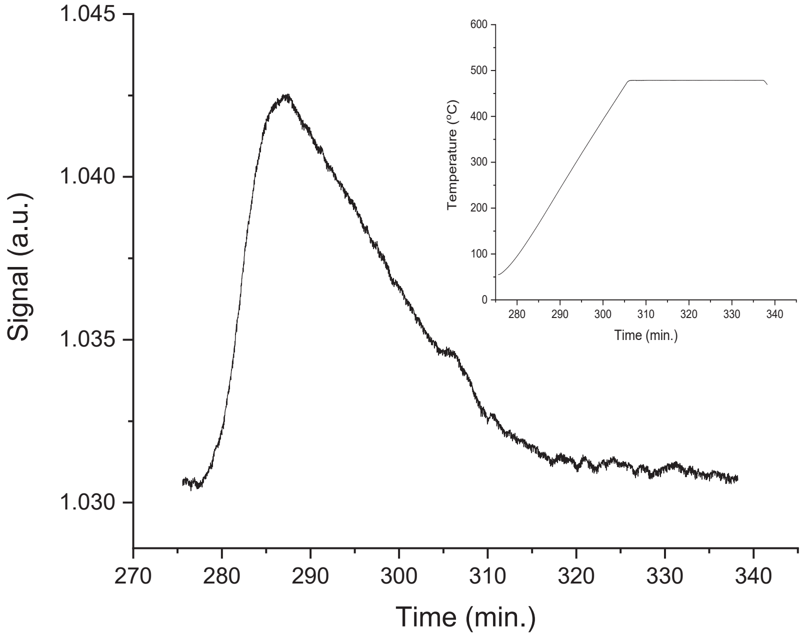

Figure A.16. The NH_3-TPD profile of 25Si75Al900-ZS catalyst