1-OCTANOL DEHYDRATION ON Al_2O_3-SiO_2 CATALYST

A Thesis Submitted to the Graduate School of Engineering and
Sciences of İzmir Institute of Technology in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

in Chemical Engineering

by
Beyza UÇAR

December 2021
İzmir

ACKNOWLEDGEMENTS

First of all, I would like to give my thanks to Prof. Dr. Erol ŞEKER who is my supervisor and my mentor, for his encouraged behaviour, support, guide, valuable remarks and teaching methods each step of this thesis. I also would like to express my sincere gratitude to my committee members.

I warmly would like to thank the members of our research group for their support, helps and friendship. Especially, I want to express my special thanks to Emre DEĞİRMENCİ for his devotion, because this thesis would not have taken its present form without him. Also, this master thesis was prepared with motivation and belief of my dear friends, specially Ecem TARANCI.

My deepest gratitude goes to UÇAR family for their support, beliefs, love and labour during my educational life. I could not be who I am today without you.

ABSTRACT

1-OCTANOL DEHYDRATION ON Al_2O_3-SiO_2 CATALYST

In this study, the effect of heterogeneous acid catalysts was investigated to product distribution by 1-octanol dehydration. The utilized catalysts were synthesized by sol-gel method. The synthesized solid acid catalysts were Al_2O_3-SiO_2, whose mass ratios were 25%-75%, 50%-50% and 75%-25%. Also, the calcination temperatures of synthesized Al_2O_3-SiO_2 catalysts were 500℃, 700℃ and 900℃. The aim of this study, understanding the acidic-basic properties of the Al_2O_3-SiO_2 catalysts and its impact on the dehydration of primary alcohol (1-octanol). For the usage of whole catalysts, the dehydration reaction proceeded on 150℃ and the reaction time was 4 h. The products and their existence amounts were determined by GC-MS analysis. Furthermore, the acidic and basic properties of the catalysts were clarified by NH_3-TPD and CO_2-TPD analyses.

This study presented that the composition of the catalysts and applied calcination temperatures had impact on acidic-basic strengths which affects pathways of the reaction. The result of that, product distribution and overall conversion were evaluated. The main products were oxalic acid 2-ethylhexyl tetradecyl ester (possible product), octyl ether, esters (Formic acid, octyl ester, Acetic acid, octyl ester and Heptanoic acid, octyl ester) and octanal. The product distribution was principally presented depending on the acidic and basic strengths of Al_2O_3-SiO_2 catalysts.

ÖZET

Al_2O_3-SiO_2 KATALİZÖR ÜZERİNDE 1-OKTANOL DEHİDRASYONU

Bu çalışmada, heterojen asit katalizörün 1-oktanol dehidrasyonunda, ürün dağılımına etkisi araştırılmıştır. Kullanılan katalizörler sol-jel yöntemiyle sentezlenmiştir. Sentezlenen katı asit katalizörler ağırlıkça farklı oranlarda (25%-75%, 50%-50% ve 75%-25%) Al_2O_3-SiO_2 katalizörleriydi. Ayrıca, sentezlenen Al_2O_3-SiO_2 katalizörlerin kalsinasyon sıcaklıkları 500℃, 700℃ ve 900℃ idi. Bu çalışmanın amacı, Al_2O_3-SiO_2 katalizörlerin asidik-bazik özelliklerini ve birincil alkol dehidrasyonu üzerindeki etkisini anlamaktır. Kullanılan bütün katalizörler için dehidrasyon reaksiyonu 150℃ ve reaksiyon süresi 4 saat olarak devam etti. Ürünler ve var olan miktarı GC-MS analizi ile belirlenmiştir. Buna ek olarak, katalizörlerin asidik ve bazik özellikleri NH_3-TPD ve CO_2-TPD analizleri ile açıklanmıştır. Ayrıca katalizörlerin kristalografisi, XRD sonuçlarına göre belirtilmiştir.

Bu çalışma, katalizörlerin bileşiminin ve uygulanan kalsinasyon sıcaklıklarının, reaksiyon yollarını etkileyen asidik-bazik kuvvetleri üzerinde etkili olduğunu ortaya koymuştur. Bunun sonucunda ürün dağılımı ve genel dönüşüm değerlendirilmiştir. Ana ürünler oksalik asit 2-etilheksil tetradesil ester, oktil eter, esterler (Formik asit, oktil ester, Asetik asit, oktil ester ve Heptanoik asit, oktil ester) ve oktanal idi. Ürün dağılımının esas olarak Al_2O_3-SiO_2 katalizörlerinin asidik ve bazik güçlerine bağlı olduğu gösterildi.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Environmental pollution has been taken attention in the worldwide because of non-renewable resources, such as carbon-based smoke emission in automotive industry. Thus, nontoxic renewable materials are required such as ether is clean biofuel [1]. The previous researches were presented that C_3 and heavier alcohols can be utilized to produce olefin and ethers, which have significant importance as fuel additives and fine chemical industry, by alcohol dehydration process [2, 3]. However, there is consequences of the alcohol dehydration in the liquid phase. The dehydration reactions produce water as a side product, so it leads to side reactions and inhibits the applied catalyst [4, 5]. Moreover, the usage of high chain alcohols leads to decrease yield due to their molecular weight [6]. Hence, these possible problems are taken attention to investigate by developed approaches.

Alcohol dehydration reaction proceeds over acid catalysts. The latter, alcohol dehydration reaction is generally used, and it requires a solid acid catalyst for efficiency because of the final separation step of homogeneous acid catalyst [1, 7]. The dehydration mechanism generate removal of OH and adjacent H over acid catalysts, that acid catalysts are responsive to the Lewis acid sites [8, 9]. Therefore, the stability, selectivity and reusability are required from the acid catalyst. The applied acidic catalysts can be resins, clays, zeolites, grafted silica samples and alumina based for alcohol dehydration reaction [2, 10]. In addition to that, zeolites, ion exchange resins and metal oxides are decided that the most favourable catalyst types for industrial dehydration [4].

Zeolites are mentioned as shape and size selective catalysts which have well-defined crystalline structures. Furthermore, they provide high activity, selectivity, thermal stability and chemical durability [4, 11]. Even though the mentioned high characteristic properties, internal and external forces can limit activity of the reaction with occurred side products [12, 13].

For the resin application as an acid catalyst, the reaction occurs at liquid phase. Although the resins are studied in various researches and observed presenting high efficiency for this process, the resins are inhibited by water because of increasing water amount during reaction. Whereas the alumina catalysts are found more stable and indicated no degradation contrary to resins, even though showing lower efficiency [2, 10, 14]. Thus, the alumina catalysts are promising more effective application with some improvements.

Alumina catalysts are defined low cost, effective, selective, stable, long lifetime, and robust acid catalysts. Moreover, they have high surface area and high porosity which are required for effective performance. Beside its good properties, it has low acidity for dehydration reaction, and it needs to be improved for product distribution. The reaction proceeds on Lewis acid sites of the catalyst to get desired product, but if the catalyst shows very strong acidic sites, it causes to producing olefins instead of ethers [1, 2, 15].

Silica gels are defined as an amorphous solid. Therefore, they have silanol groups (SiOH) on its surface. The property of silanol groups is weak acidic and weak basic, and also it is capable of adsorbing water. Most of the adsorbed water can be removed by drying in the air. The previous investigations are showed that silication of alumina catalyst improves property of the catalyst for dehydration process. It increases the acidity and acidic strength of the Lewis acid sites. Furthermore, the silanol groups of silica prevent inhibition of the catalyst due to water existence [4, 16-18]. Thus, the silica-alumina catalysts are bifunctional effective catalysts for the alcohol dehydration.

It is well known fact that there are various types of methods such as sol-gel, precipitation, impregnation, etc. for catalyst synthesis with supporting reagents [18]. The sol-gel technique is taken attention because of the advantageous. This technique offers high surface area with strong bonds between the molecules, controllable pore size distribution, high purity, great thermal stability, and advanced activity for functionalized catalysts [18-20]. The sol-gel method is based on generation of stable colloidal solution, and the latter condensation of the colloidal particles to get polymeric chains. The colloidal solution can be obtained by existence of water or alcohol with electron donor substituent. The hydrolysis-condensation of organic metal alkoxides is generally favoured, and the silica and alumina are mostly used for colloidal particles. In this method, there are three main synthesis strategies, which are precipitation, co-condensation, and co-gelation, to achieve stabilization of the material. Furthermore, the synthesis strategies depend on chemistry of the phase and matrix precursors [21].

The alcohol dehydration reaction gives olefins and water as main products. Therefore, when the chemical properties of primary, secondary and tertiary alcohols are investigated, the secondary alcohols are found with high yield to produce olefins which can lead to produce ethers in further. The primary alcohols are given poor yield because of unhidden hydroxyl groups. Thus, they are found prone to give reverse reaction whose route is from olefins to alcohols [5]. Whereas the produced water is mentioned that it causes to side reactions with applied acid catalyst. These side reactions are hydration, esterification, and further ester hydrolysis. Furthermore, if the applied catalyst has both acidic and basic sites, dehydrogenation and oxidation reactions are possible to occur [4, 5, 22]. The possible products of these reactions are olefins, ethers, carboxylic acids, esters, aldehydes, and ketones.

The alcohol dehydration reaction produces olefins. The olefins are important feedstocks for fine chemical products. They can be used to produce linear low-density polyethylene which is a starting material for lubricant and polyolefin synthesis and plasticizer alcohols. The usage of long chain olefins improves tensile strength, puncture strength, and cracking resistance for polyolefin production [23, 24].

The bimolecular dehydration reaction of alcohols produces ethers. Especially, the primary alcohols give good yield because of unhindered hydroxyl groups [5]. Also, ethers can be produced from olefines and glycols over acid catalysts [2, 10, 25]. The obtained ethers are mostly used as a fine chemical in cosmetic industry and fuel additive in automotive industry [9, 26]. The ethers lead to increase cetane number of the fuel blends, improve cold flow properties, and reduce CO, Sulphur content and smokes in the releasing gas of the vehicles [2, 3, 27, 28]. Nevertheless, these ethers can be used for production of olefins which are important feedstock in chemical industry, for example, lubricant and polyolefin production [23].

The dehydrogenation and oxidation reactions of alcohols produce aldehydes and ketones. The further oxidation produces carboxylic acids. Especially, aldehydes and carboxylic acids contribute to progress lubrication in diesel fuel. Moreover, alcohol and carboxylic acid produce alkyl esters by Fischer esterification process. These esters can be used the industrial production of paints, solvents, cosmetics, and medicines [2, 5, 29].

In this study, the utilization of 1-octanol is decided for alcohol dehydration process, due to final valuable products from long chain alcohols. Furthermore, the Al_2O_3-SiO_2 catalyst is decided to synthesize as an amorphous solid acid catalyst for 1-octanol dehydration process. The effect of acidic and basic properties is aimed to understand on alcohol dehydration reaction. The reaction proceeded in liquid phase. Thus, the product distribution, possible side reactions, and the properties of the synthesized catalyst which are efficiency, selectivity, acidity, pore size, stability are investigated.

CHAPTER 2

LITERATURE SURVEY

2.1. The Acid Catalysts for Alcohol Dehydration Reaction

In this part, different investigations are presented over various type of acid catalysts. This part split into three main categories according to type of the catalysts which are commonly used for alcohol dehydration reaction.

2.1.1. Ion exchange resins

Guilera et al. investigated ethyl octyl ether (EOE) production over various type of resins. The EOE was decided as final product due to its beneficial properties on the fuel industry (i.e., reducing air pollutants, increasing the cetane number etc.). The decided reactants were diethyl carbonate (DEC) and 1-octanol. The carbonates were utilized to make more efficient the alcohol dehydration reaction. The DEC was produced from the ethanol (Figure 1 and Figure 2), and further it was converted to produce EOE (Figure 3) [30].

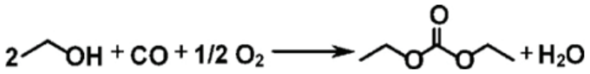

Figure 1. Alcohol dehydration reaction with carbonate to produce EOE [30].

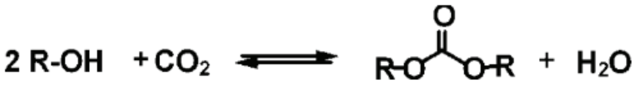

Figure 2. CO_2 and alcohol react to produce DEC [30].

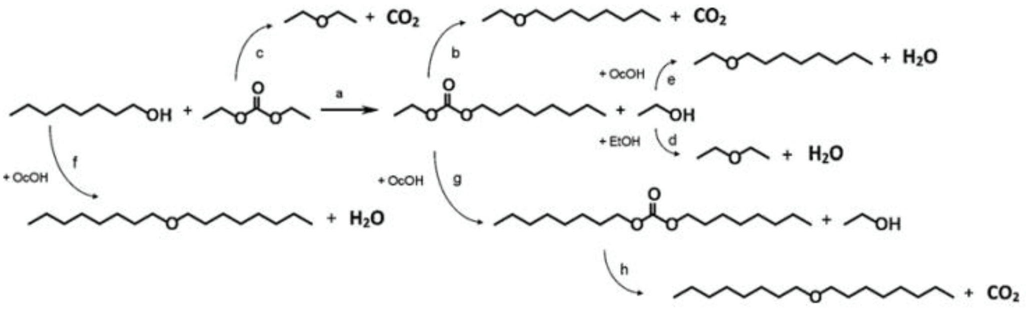

Figure 3. Reaction pathway of EOE production from 1-octanol with DEC [30].

The explanation of the Figure 3, c path was undesired because of further consumption of diethyl carbonate. The g and h paths were presented as by-products (ethyl octyl carbonate and dioctyl carbonate). Beside the decomposition of carbonate, linear ether production routes were presented by d, e and f pathways [30].

Diethyl ether (DEE) and di-n-octyl ether (DNOE) were elected as side products. Although, the DNOE had sufficient properties on the diesel fuel, the DEE had serious consequences due to its high volatility. Therefore, the acid resins were mentioned that they tent to produce short chain ethers which are not suitable for oil industry, besides that they were sensitive to water inhibition [30].

The tested catalysts were Amberlyst 15, Amberlyst 16, Amberlyst 21, Amberlyst 26, Amberlyst 35, Amberlyst 36, Amberlyst 39, Amberlyst 46, Amberlyst 48, Amberlyst 70 and Amberlyst 121, and Purolite (CT124 and CT224), Sigma (Dowex 50Wx8-100, Dowex 50Wx2-100 and Nafion NR-50 as acid resins. The resins were crosslinked with low divinylbenzene (DVB) to get more flexible structure. The structure information and properties of the resins were given in Table 1 [30].

Table 1. Properties and structural parameters of the resins [30].

Catalyst	Short Name	Type	DVB %	Acidity (m_{eq} H^+/g)	V_{sp} (cm^3/g)	S_{BET} (m^2/g)	d_p (mm)	T_{max} (^oC)
Amberlyst 15	A 15	M	20	4.81	0.823	42.01	0.65	120
Amberlyst 35	A 35	M	20	4.80	0.736	28.9	0.66	150
Amberlyst 48	A 48	M	High	5.62	0.563	33.8		
Amberlyst 46	A 46	M	High	0.43	0.16	57.4	0.78	120
Amberlyst 16	A 16	M	12	4.80	1.245	1.69	0.56	130
Amberlyst 36	A 36	M	12	5.40	0.999	21.0	0.57	150
Amberlyst 39	A 39	M	8	5.00	1.451	0.09	0.54	130
Amberlyst 70	A 70	M	8	3.01	1.189	0.02	0.55	190
Amberlyst 121	A 121	G	2	4.80	3.263	0.02	0.44	130
Nafion NR-50	Nafion 50	G		0.89		0.35	2.40	180
Dowex-50Wx8-100	Dow 8	G	8	4.83	1.627	0.23	0.17	150
Dowex-50Wx2-100	Dow 2	G	2	4.83	2.655	1.32	0.25	150
CT124	CT124	G	4	5.00	1.994	0.07	0.76	
CT224	CT224	G	4	5.34	1.811	0.95	0.33	150

[BET surface area in dry state (N_2 for $S_{BET} \geq 1$ m^2/g; Kr for $S_{BET} < 1$ m^2/g). M = macroreticular; G = gel-type. Amberlyst 46 was sulfonated only at the polymer surface. Amberlyst 70; chlorine substituting hydrogen atoms in polymer chains. V_{sp}; volume of swollen polymer]

The observations proved the importance of acidic property on the efficiency. The experiments were presented while the acidity of catalyst increased, the EOE synthesis and decomposition of DEC increased too. Whereas the low acidity caused to low EOE yield.

Furthermore, EOE is a large ether type, and the investigators decided high acidity, low DVB content and expanded polymer network were necessary to synthesis of long chain linear ether. The final contents were high amount EOE (60 mol%), and side products DEE (20 mol%) and DNOE (20 mol%), also Dowex 50Wx2-100, Amberlyst 121 and CT224 were found responding to the requirements [30].

Bringue et al. worked similarly for dehydration of 1-octanol to di-n-octyl ether in liquid phase (Figure 4). The tested catalysts were DVB based gel type and macroreticular acidic resins which were Amberlyst 15 (A 15), Amberlyst 16 (A 16), Amberlyst 35 (A 35), Amberlyst 36 (A 36), Amberlyst 39 (A 39), Amberlyst 46 (A 46), Amberlyst 70 (A 70), Purolite (CT-175, CT-224, CT-252 and CT-276) and Dowex 50Wx4 (DOW50Wx4). The reaction was proceeded in a batch reactor with the system of water removal, and the products were mainly analyzed by gas chromograph [31].

Table 2. DNOE properties as diesel fuel [31].

	Diesel fuel	DNOE
Density at 288–293 °C (kg/m^3)	850	806
Boiling point (K)	443-653	559
Viscosity (cSt)	3-1	
Cetane number* (−)	48-51	119
Cloud Point* (K)	271-278	256
Cold Filter Plugging Point* (K)	269-276	258

[*Blending values.]

The tested resins were examined according to their morphology of polymer skeletons due to their swelling. Swelling was mentioned as a key parameter which used to describe porosity of the catalyst. The swollen states were detected by Inverse Steric Exclusion Chromatography (ISEC). Despite the fact that producing water is a troublemaker, a little amount of it was found to assist swelling of catalyst that lead to modify accessible acid sites and improve yield of the product [31].

Microporous resins such as CT-224 were defined its reaction produce ether as a main product. Also, the reaction was not proceeded when the whole alcohol was consumed in the system. Whereas macroreticular resins (i.e., A 36) were showed the leaning run on the reaction by decomposition of DNOE to form olefin and its isomers (Figure 5). For macroreticular resins, over sulfonation were focused to evaluate its effect on DNOE formation. The performed experiments presented over sulfonation was not favor the DNOE formation due to hinder acid sites, cause to increase formation of water. The best DNOE yield was observed by gel type resins with low DVB such as CT-224 (Table 3) [31].

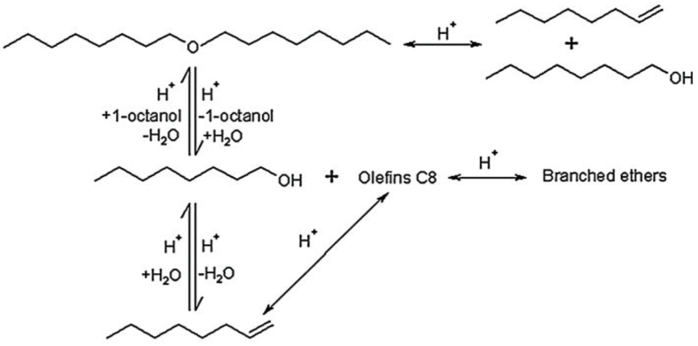

Figure 4. Reaction mechanism for the dehydration of 1-octanol to DNOE [31].

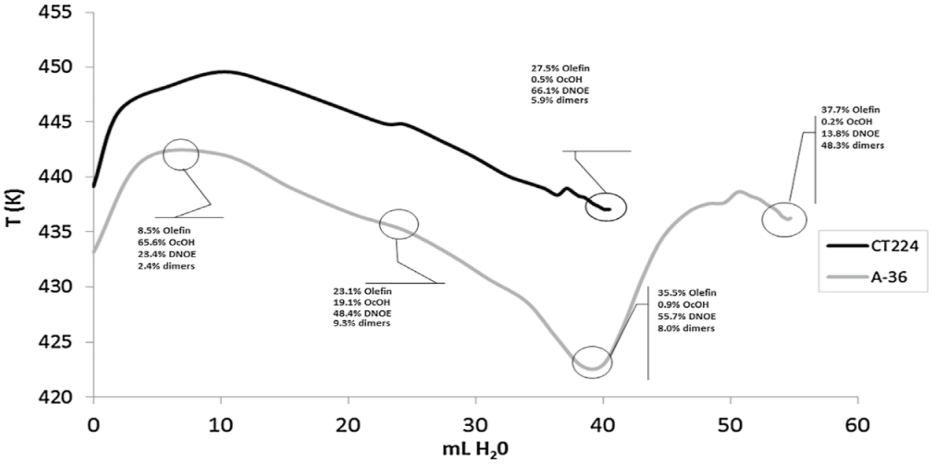

Figure 5. Temperature progression of the system after removal of water 7 h and 9 g of catalyst for CT224 (━) and A 36 (▬) at atmospheric pressure [31].

Table 3. The achieved selectivities (S) and yields (Y) for whole tested resins after 7 h on 9 g of resin at boiling point and atmospheric pressure [31].

Catalyst	$X_{1\text{-octanol}}$ (%)	S_{DNOE}	$S_{Olefins}$	S_{Dimers}	$S_{Bethers}$	Y_{DNOE}
A 15	100	44.2	38.7	17,1	-	44,2
A 16	100	49.4	26,30	24,3	-	49,4
A 35	100	17,40	32.9	49,6	-	17,4
A 36	100	13,20	39.1	47,7	-	13,2
A 39	100	48.1	27,40	24,5	-	47,8
A 46	59	85.6	10,60	-	3,8	49,6
A 70	100	53.7	30,10	16,2	-	53,5
CT-175	100	44.6	27..8	27,6	-	44,6
CT-224	100	63.1	28,30	8,6	-	62,8
CT-252	100	45.9	25,40	28,6	-	45,9
CT-276	100	37.2	27,80	34,9	-	37,1
DOW50Wx4	100	54.7	26,40	18,9	-	54,6

Gray et al. focused on supercritical conditions with $scCO_2$ that was chosen solvent for experiment by usage of Amberlyst 15 to form ethers. The reason of decided solvent was explained with high solubility of ether products in $scCO_2$ and easy separation from water to prevent undesired reactions, and also the supercritical solvent influenced the yield but not selectivity. Furthermore, the n-alkyl ethers were obtained with high yield from primary alcohols, while secondary alcohols were producing olefins and branched ethers. A continuous flow reactor was applied for the experiment. Amberlyst 15 showed high yield but had low thermal stability. Although, the application of continuous reactor indicated satisfied output, it was not suitable for large scale production due to dealing with high pressures [7]. Thus, the investigation set forward a laboratory scale beneficial work for acid resin with continuous reactor.

Casas et al. studied dehydration of 1-octanol to form DNOE by Amberlyst 70. The Amberlyst 70 was defined a macroreticular resin, thermally stable and having low DVB crosslinking degree. 1,4-dioxane was used as a solvent to prevent phase difference between water and alcohol during the reaction, and the reaction proceeded in a batch reactor. The inhibitor effect of water was observed when its value increases in the mixture. It blocked the active sites. Additional observation was the reaction rate increased with increasing temperature and decreased with releasing water. The adsorption-reaction-desorption process considered, and the surface reaction assumed as a rate limiting step. The necessary kinetic equations based on Langmuir Hinshelwood Hougen Watson-Eley Rideal (LHHW-ER) mechanisms to rate data. Thus, appropriate rate of the reaction was predicted. The activities of 1-octanol, DNOE and water were calculated by the UNIFAC-DORTMUND predictive method. This method assisted to find optimum work conditions. The best reaction model was decided where 1-octanol adsorbed to the resin surface with another 1-octanol in liquid phase get into the reaction to form DNOE based on ER mechanism (Figure 6) [27].

$$\begin{aligned}
&1-\mathrm{OcOH}+\sigma \rightleftarrows 1-\mathrm{OcOH}\cdot\sigma\\
&1-\mathrm{OcOH}\cdot\sigma+1-\mathrm{OcOH} \rightleftarrows \mathrm{DNOE}\cdot\sigma+\mathrm{H_2O}\\
&\mathrm{DNOE}\cdot\sigma \rightleftarrows \mathrm{DNOE}+\sigma
\end{aligned}$$

Figure 6. The best reaction model to form DNOE based on ER mechanism [27].

Perez et al. worked dehydration of 1-butanol to di-n-butyl ether (DNBE) by utilizing various types of ion exchange resins (Table 4). During the dehydration process, ether and olefin was observed as main products. Once the olefin formed, it is possible to convert to secondary alcohol with a side reaction. The olefins were mostly selective to form ether by hydrolysis. The most active resin was Amberlyst 36 with 23.2% conversion, and the most selective resin was Amberlyst 121 with 99.1%. Amberlyst 15 and Amberlyst 31 was found losing their acid sites by leaching in the reaction. Besides, the researchers looked for the effect of impurity in the 1-butanol. For that aim, 2-methyl-1-propanol was added as an impurity to the 1-butanol. The experimental results showed that olefin production did not be affected by impurity, but ether isomerization was observed [32].

Table 4. The utilised ion exchange resins and their properties [32].

Catalyst	Short name	Structure[a]	DVB%	Sulfonation type[b]	Acidity[c] (m_{eq} H^+/g)	Tmax[d] (◦C)
Amberlyst 15	A-15	M	20	M	4.81	120
Amberlyst 35	A-35	M	20	O	5.32	150
Amberlyst 16	A-16	M	12	M	4.8	130
Amberlyst 36	A-36	M	12	O	5.4	150
CT482	CT-482	M	Medium	M	4.25	190
Amberlyst 70	A-70	M	8	M	2.65	190
Amberlyst 39	A-39	M	8	M	5	130
Dowex 50W×8	DOW-8	G	8	M	4.83	150
Amberlyst 31	A-31	G	4	M	4.8	130
Dowex 50W×4	DOW-4	G	4	M	4.95	150
Amberlyst 121	A-121	G	2	M	4.8	130
Dowex 50W×2	DOW-2	G	2	M	4.83	150
Amberlyst 46	A-46	M	High	S	0.87	120

[[a] Macroreticular structure (M) or gel-type structure (G). [b] Monosulfonated (M), oversulfonated (O) or sulfonated only at the polymer surface (S). [c] Titration against standard base following the procedure described by Fisher and Kunin]

Generally, the ion exchange resins presented satisfying properties such as efficiency, selectivity, activity etc. Nevertheless, the researchers could not avoid the problem of water existence. Thus, an alternative developed catalyst needs still continued.

2.1.2. Zeolites

Hoek et al. investigated ether synthesis from 1-octanol over zeolite BEA (SiO_2-Al_2O_3). They decided zeolite was a comparable catalyst for dehydration process due to the thermal instability of ion exchange resins. Therefore, the properties of zeolite BEA given in Table 5. The water effect was investigated either open system (water removed) or closed system (water exist). Gas chromatograph analysis was utilized for catalyst characterization [33].

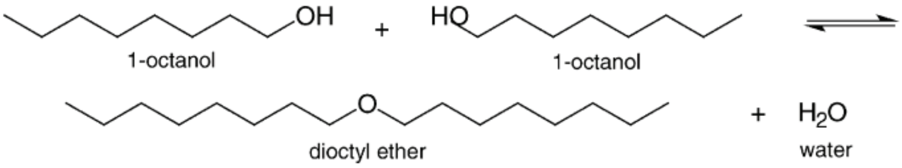

Figure 7. The dehydration of 1-octanol to di-octyl-ether [33].

Table 5. Properties of the zeolite BEA catalysts [33].

	Particle size d_p (m)	Surface area S_{BET} (m^2/g)	Pore volume V_{pore} (ml/g)
BEA extrudates	$3x10^{-3a}$	580	0.9
BEA powder	$8x10^{-3b}$	640	1.1

a Diameter of extrudates.

b Size of the crystal clusters.

For zeolite BEA, the effect of particle size was examined the results showed that even powder application had better activity there was no significant change between the ground extrudates. Thus, the researchers decided particle effect was ignorable and no internal mass transfer limitations. Furthermore, the reaction proceeded at 390, 400, 420, and 430 K to find activation energy which was 149.8 kJ/mol from the graphical result. The Langmuir–Hinshelwood method was used for the description of reaction kinetics. Besides, the influence of catalyst concentration did not show any inhibiting effect on active sites. In spite of that, the empty catalyst sites and initial reaction rate decreased when the concentration of alcohol increased. That presented its inhibiting effect because the alcohol molecule needed empty catalytic site for conversion and separation of water. For closed system, water caused inhibitory effect owing to occurring two different reactions which were adsorption of water on the H^+ sites and forming the H_3O^+ sites after the adsorption. Nevertheless, the researchers concluded the vast examinations were needed to find more accurate results for the negative effects of water existence [33].

Veiga et al. worked on ether synthesis from various glycols, ethanol, and 1-octanol over acid zeolites. The acid catalysts were USY series, H-Beta and HZSM-5 zeolites which are silica-alumina based catalysts, and the reactant materials were glycerol, 1,2-propylene glycol or ethylene glycol with ethanol or 1-octanol for ether synthesis. The density and strength of acid sites were identified by Temperature-Programmed Desorption (TPD). Temperature-programmed desorption unit was used to measure the hydrophobicity index of the zeolites. Also, the product characterization was determined by gas chromatograph with mass spectroscopy. The experiments were performed in a batch reactor, and mono ether production aimed with etherification reaction [10].

Si/Al ratios in bulk or framework and the amount of eliminate extra framework aluminium (EFAL) were showed extra importance on the determination of acidic performance in catalysts (Table *6*). The bulk Si/Al molar ratio presented adsorption sites (Brønsted and Lewis acid sites). Zeolites, which had higher bulk Si/Al molar ratio (11.2–12.3), showed higher hydrophobicity index that means higher acidity. Thus, aluminium content had an effect on acidic property of the catalyst. USY-650-L-2, H-Beta, and HZSM-5 were found having higher bulk Si/Al molar ratio that leaded to higher glycol conversion for etherification. Furthermore, while the low aluminium content leaded to low acid site density and high hydrophobicity which induced to weak adsorption of glycerol, the high aluminium content caused to polarization of the surface due to high acid site density which obstructs the reaction. For ethylene glycol investigation, USY-650-L-2, H-Beta and HZSM-5 zeolites showed better conversion for production of mono and diethyl ethers. Also, HZSM-5 was decided for having the best performance for that. Therefore, etherification of ethylene glycol and 1-octanol investigation indicated that 2-octyloxy ethanol production had an important role for mono ether production which occurs by auto-etherification. The 2-octyloxy ethanol was the main product for HZSM-5 (64%). USY-650-L-2 and H-Beta leaded to produce 1,1-oxybis octane which was side product for the process, and HZSM-5 produced that as minimum. Thus, HZSM-5 zeolite decided the best catalyst. The best reaction conditions for 2-octyloxy ethanol, which converted to mono ether, were when 1-octanol/ethylene glycol molar ratio was 4, catalyst weight 10 wt. % for USY-650-L-2 and HZSM-5 zeolites, and 5 wt. % for H-Beta zeolite. Therefore, the best ethylene glycol conversion was achieved over HZSM-5 zeolite (61%) with comparing to USY-650-L-2 (59%) and H-Beta (59%). Moreover, the highest amount of 2-octyloxy ethanol was synthesized over HZSM-5 zeolite (74%) [10].

Table 6. Chemical composition of USY, H-Beta and HZSM-5 zeolites measured by different techniques [10].

Catalyst	$(Si/Al)_{bulk}$	$(Si/Al)_{framework}$		EFAL (%)
	(a)	(b)	(c)	(b)
USY-550	2.8	4.9	5.6	43
USY-550-L	3.4	5.3	6	3.6
USY-650	2.8	5.7	5.3	52
USY-650-L	3.9	6.3	8	38
USY-650-L-2	1.2	13.3	15.5	17
H-Beta	12.3	n.d.	16.4	n.d.
HZSM-5	12.3	n.d.	12.5	n.d.

(a) XRF.

(b) ATR.

(c)^{27} Al MAS-NMR.

n.d.= not determined.

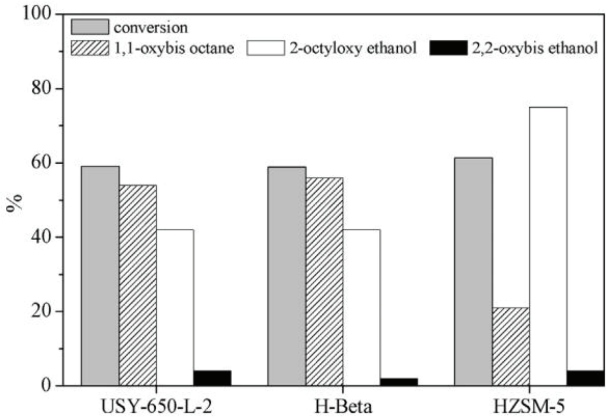

Figure 8. the etherification reaction of ethylene glycol and 1-octanol. Experimental conditions: reaction temperature = 200 °C; 1-octanol/ethylene glycol molar ratio = 4; reaction time = 6 h; stirring velocity = 600 rpm; catalyst concentration = 10 wt. % for USY-650-L-2 and HZSM-5 zeolites, and 5 wt. % for H-Beta zeolite [10].

Song et al. investigated the dehydration of 1-octadecanol over silica-alumina based zeolite which was H-BEA. They tried to understand the impact of Lewis acid sites and Brønsted acid sites on the activity. The H-BEA was mentioned as a microporous catalyst. It is well known fact that, zeolites are shape selective catalysts. Thus, the researchers aimed to investigate pathway selectivity too. For that aim, they utilized the density functional theory (DFT) and the experimental studies. The 1-octadecanol was observed to blocking acid sites on the catalyst because of having long alkyl chain. The intramolecular dehydration product was octadecene, and this reaction cause to increase Brønsted acid sites. The intermolecular dehydration produced dioctadecyl ether. Also, the intermolecular dehydration was decided with lower energy need to run due to low activation energy barrier. The production of dioctadecyl ether was observed pore mouth and surface of the catalyst. Further works showed that if the temperature increased, the product distribution turned to octadecene instead of dioctadecyl ether by cleavage of intermediate dioctadecyl ether. Besides, the various Si/Al ratios of H-BEA catalyst was investigated, and the best yield was achieved on 75% Si/Al for octadecene production (Figure 9). In addition to that, the catalyst poisoned with quinoline, and it presented the effect of decreasing Lewis acid sites. The low acid sites were adequate to produce ether, but not enough to form octadecene and cleavage of the ether. The Brønsted acid sites and Lewis acid sites took a role to form octadecene, because dioctadecyl ether was able to contribute octadecene formation in further. Thus, the location of acid sites was loosed the interest on alkene formation, and the importance of strong acid sites was understood to form alkene [34].

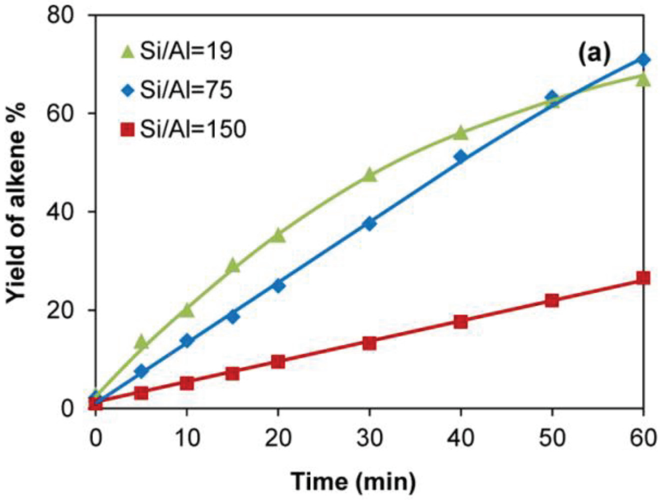

Figure 9. The dehydration of 1-octadecanol to octadecene over H-BEA zeolite with various Si/Al ratios as a function of time [34].

Even the different methodologies were followed in the researches. The requirements of the necessary catalyst for olefin and ether production were the same. Furthermore, the Lewis acid sites had an important role for the production of olefins and ethers. The observations showed that the water existence inhibited the catalysts and prevented occurring desired products during the reactions.

2.1.3. Solid Metal Oxide Catalysts

Garbarino et al. investigated DEE production from ethanol, as well as ethylene formation from ethanol by cracking of ethoxy groups and by cracking of DEE. For this work, commercial alumina (γ-Al_2O_3 (PTH)) and lanthanum-doped alumina (La-γ-Al_2O_3~ 1% wt. (PL1) and 4% wt. (PL4)) was used as acid catalysts. The lanthanum doping was mentioned that it improves alumina properties in some ways such as mechanical strength and stability. Moreover, X-Ray diffraction (XRD), skeletal IR and Field Emission Scanning Electron Microscopy (FE-SEM) was utilized to characterize the materials. Experiments were performed the steady state flow reactor and the temperature programmed surface reactions [35].

According to experiments, the DEE formation was occurred at 480–520 K (Equation 1). When the temperature range was increased to 520–555 K, ethanol produced DEE (Equation 2) and ethylene (Equation 2). For further heating (555–630 K), even the reaction (1) and (2) was still continued, DEE decomposition was started to form ethanol and ethylene (Equation 3). Above 630 K, only ethylene production from ethanol was observed. The reactions and their behaviours with temperature progression over PTH, PL1 and PL4 catalysts were given in Figure 10 [35].

$$2\ CH_3CH_2OH \rightarrow (CH_3CH_2)_2O + H_2O \qquad \text{(Equation 1)}$$

$$CH_3CH_2OH \rightarrow H_2C{=}CH_2 + H_2O \qquad \text{(Equation 2)}$$

$$(CH_3CH_2)_2O \rightarrow CH_3CH_2OH + H_2C{=}CH_2 \qquad \text{(Equation 3)}$$

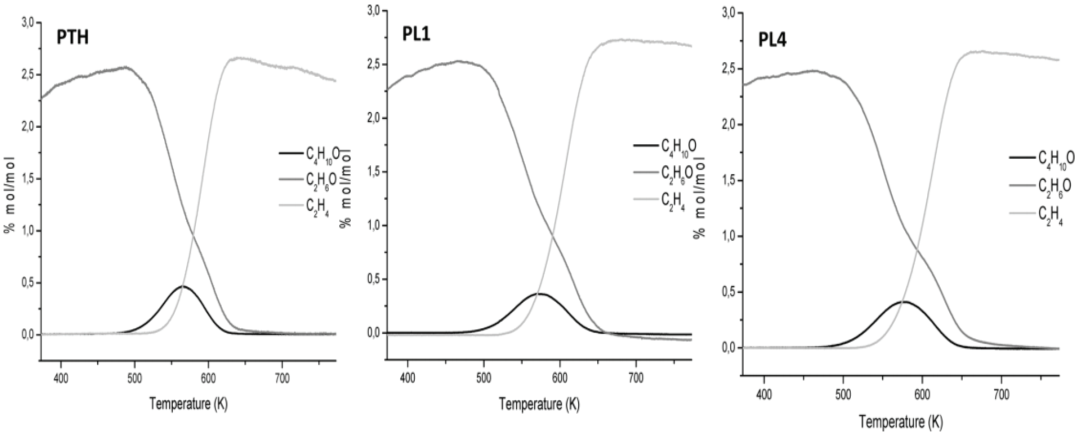

Figure 10. Ethanol Temperature Programmed Surface Reaction (TPSR) results on the investigated catalysts. Reaction conditions: catalysts mass 43 mg, total flow rate 170 ml/min (2% ethanol/98% N_2), temperature range 373–773 K, ramping rate 5 K/min [35].

Ethanol conversion was found decreasing with increasing La doping amount due to its inhibiting effect. For the formation of diethyl ether from ethanol, the major effect was detected as the reaction temperature. Therefore, γ-Al_2O_3 submitted high activity for this process. Whereas Lewis acid sites of alumina was occupied and modified by lanthanum, and also La_xO_y clusters were observed by overloading of lanthanum. These leaded selective poisoning on Lewis acid sites. Even though the number of acid sites changed by lanthanum, the lanthanum had significant effect to reduce coking and increase stability of catalyst for the reactions. DEE formation from ethanol was identified over 70% for all samples by low temperature application [35].

Nel et al. enquired ether formation from linear primarily alcohol dehydration over η-alumina. The alumina catalyst was selected because of its strength in water existence. Therefore, η-alumina was mentioned more active and stable than γ-alumina for ether synthesis by the alcohol dehydration process. The decided alcohols were 1-pentanol (99%), 1-hexanol (98%), 1-heptanol (98%), 1-octanol (99%), 1-nonanol (98%), 1-decanol (99%), and 1-dodecanol (98%) for this study. Fixed bed reactor system was used for the experiments, and gas chromatograph with flame ionization detector (GC-FID) was applied for product characterization. Alcohol conversion with temperature (250-350 K) at approximately atmospheric pressure was examined. The results showed that increasing temperature assisted to increase alcohol conversion, and the highest conversion obtained from 1-octanol (97 mol%). 1-decanol dehydration also demonstrated highest catalyst deactivation. Selectivity of the process was decided another major issue because of the side products (olefin, aldehyde etc.). Although increasing temperature were promising higher conversion, the reaction path tended to form side products instead of ether with increasing temperature. For instance, 1-octanol was presented highest conversion but it mostly leaded to produce side products. Additionally, pressure effect was investigated, and esterification was observed as a side reaction with high pressure applications. The esters involved to form an alcohol and a carboxylic acid (Equation 4). The researchers concluded that the desired product occurred at Lewis acid sites, and Brønsted acid sites and basic oxidic sites caused to side reactions. Another conclusion was higher acid site density assisted to etherification, and stronger acid sites leaded to proceed the reaction complete. For example, α-olefins and linear ether production from alcohol dehydration, and linear α-olefin formation from the ether was given in (Equation 5, 6 and 7 respectively. Also, the reaction restriction was defined mass transfer limited. Furthermore, the highest yield was obtained from 1-hexanol (54% yield) to form ether over η-alumina at 300℃, 1 MPa, and WHSV of 1 h^{-1} [2].

$$\mathrm{R{-}CH_2{-}O{-}(CO){-}R + H_2O \rightarrow R{-}CH_2{-}OH + R{-}COOH} \qquad \text{(Equation 4)}$$

$$\mathrm{R{-}CH_2{-}CH_2OH \rightarrow R{-}CH{=}CH_2 + H_2O} \qquad \text{(Equation 5)}$$

$$\mathrm{2R{-}CH_2OH \rightarrow R{-}CH_2{-}O{-}CH_2{-}R + H_2O} \qquad \text{(Equation 6)}$$

$$\mathrm{R{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}R \rightarrow 2R{-}CH{=}CH_2 + H_2O} \qquad \text{(Equation 7)}$$

Makgoba et al. studied dehydration of alcohol (1-hexanol and 1-octanol) over silicated alumina. Alumina was decided to use because of not causing formation of ionic intermediates, and γ-alumina was mentioned as the most common catalyst for the dehydration reaction of heavy alcohols. Therefore, silica-alumina was explained with its strong acidity which leaded to isomerization reaction and decreased the selectivity of 1-alkene. The silicated alumina occurred on the Lewis acid sites, and the reactivity of the hydroxyl groups to adsorbed materials was specified by the strong Lewis acid sites. The applied temperature range was decided from room temperature to 800℃ for the silication. The temperature ranges of the dehydration process were decided 280-325℃ for 1-hexanol, and 280-330℃ for 1-octanol. The reactions were performed in a fixed bed reactor. Analysis of the materials was made by Inductively Coupled Plasma (ICP) Spectroscopy [17].

The experiments run on 1-hexanol to form 1-hexane, and γ-alumina demonstrated high selectivity over the reactions. Dihexyl ether amount perceptibly decreased to form 1-alkene with existence of γ-alumina catalyst. The observations proved that 1-hexane purity was 95-97% where the conversion of 1-hexanol under 80% (Figure 11). The reactions were performed on long periods (time on stream (TOS)). The sharp difference occurred, while 1-hexane purity was decreasing with time (from 96.2 to 89.6% after 261 h), the isomerization of 1-hexane increased. The reason explained with increasing acidity of the catalyst. Furthermore, the same results were obtained 1-octanol conversion over γ-alumina under same operating conditions [17].

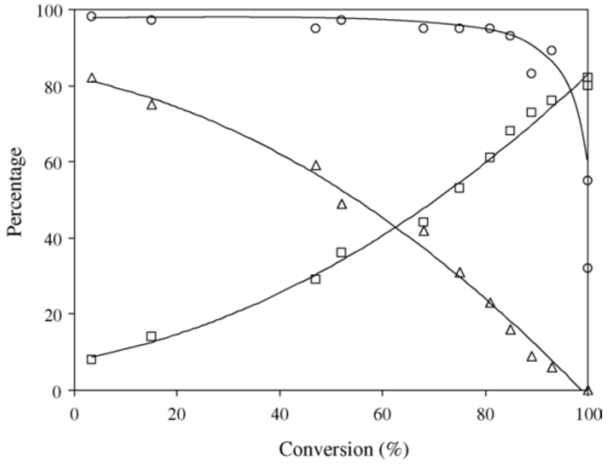

Figure 11. Selectivity to ether (△), hexenes (□) and 1-hexene purity (○) as a function of conversion for the dehydration of 1-hexanol over γ-alumina [17].

Another given challenge is that the feed alcohol stream included silica, and the fresh catalyst had close approximately to 200 ppm silica content. The experimental results were indicated the silica content accumulated for both 1-hexanol and 1-octanol dehydration processes in the reactor and on catalyst surface. Thus, the accumulated silica leaded to decreasing selectivity and rising acidity of the catalyst. The result of that, undesired products occurred more than acceptable amount such as iso-alkenes. The silica content was detected more over 15 times of the feed ingredient for both dehydration of alcohol experiments (Table 7 and Table 8). In the meanwhile, even the alcohol feed was included less than 1 ppm silica, the problem of accumulated silica continued. To sum up of this investigation, the researchers revealed the negative effects of silica on the applied reaction and γ-alumina in their study [17].

Table 7. ICP analysis of the fresh and used γ-alumina catalysts from the dehydration of 1-hexanol at 300℃ and 8 h^{-1} [17].

Catalyst	Total TOS (h)	BET (m^2/g)	Trace elements (ppm)				
			Si	Fe	Na	Ca	K
Fresh	0	235	186	199	142	154	<10
Used	261	221	2723	196	146	173	<10
Regenerated and re-used (120 h)	381	223	3112	243	190	165	<10

Table 8. ICP analysis of the fresh and used γ-alumina catalyst from the dehydration of 1-octanol at 280℃ and 10 h^{-1} [17].

Catalyst	TOS (h)	Trace elements (ppm)				
		Si	Fe	Na	Ca	K
Fresh	0	194	175	135	139	<10
Used	370	2677	177	156	139	<10

Sun et al. investigated on dimethyl ether (DME) synthesis and the researchers presented a study by combining previous works on this topic. DME was defined as an intermediate product which could convert into olefins and aromatics and can be used in energy industry. The mentioned processes included two steps the first one was dehydration from methanol over solid acid catalyst (γ-Al_2O_3 and zeolite such as HZSM-5) and the second one was direct conversion from syngas. The syngas to DME process was one step and it took their attention in advance. Also, the γ-Al_2O_3 was decided to utilize because of its properties such as strength, suitable acidity, low cost, and selectivity for DME. The γ-Al_2O_3 was modified with Nb_2O_5 (10 wt.%). Even Nb_2O_5 leaded to decrease the resistance of acid sites, it assisted to increase acid sites. Besides, the γ-Al_2O_3 was mixed with χ-Al_2O_3 (20 wt.%) to enhance higher yield of DME (86%), higher stability and robustness. In spite of the obtained high catalytic performance over zeolite, it leaded to formation of coke and hydrocarbons due to strong acid sites. Thus, the various modifications were applied for development such as rare metals, alkaline metals, composite oxides etc. Thus, the decided catalyst was given Cu/ZnO/Al_2O_3 as a supported bifunctional catalyst. The advantage of Cu was explained with its high surface area, and Cu assisted to get improvements of number of acidic sites (more effective active sites), DME selectivity and catalytic activity in previous works (Figure 12). Furthermore, the zeolite capsule catalyst was expressed as a new type of well-designed catalyst. Its structure included core catalyst (Cu/ZnO/Al_2O_3) and zeolite shell (HZSM-5) which was coating the surface of the core catalyst (Figure 13). It was performed DME synthesis from methanol, and demonstrated promising for higher efficiency, selectivity, and lower by-products [15].

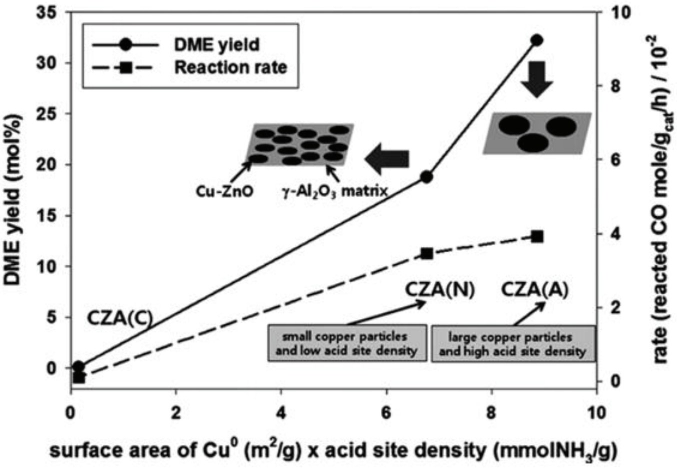

Figure 12. the reaction rate and the DME yield to the surface area of Cu with number of acidic sites [15].

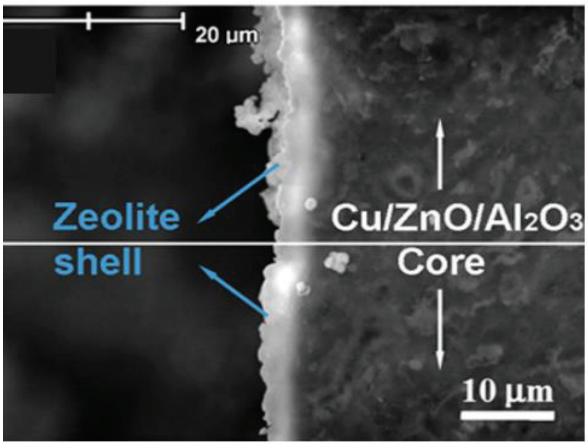

Figure 13. Cross section SEM image of zeolite capsule catalysts ($Cu/ZnO/Al_2O_3$-HZSM-5) [15].

Despite the whole type of catalyst investigation, the deactivation of catalyst during reaction the syngas to DME was inevitable. Besides, sintering of Cu was given a reason for coke formation on the dehydration of methanol. The formed water during the reaction was remained a problem on the deactivation of the catalyst. As a result, this study represented a need of designed catalyst which have better surface area, pore volume, selectivity, acidity, and suitable kinetic behaviour [15].

Chokkaram et al. investigated the dehydration of 2-octanol over alumina, nickel-alumina, and cobalt-alumina catalysts which are weak acidic catalysts. The nickel-alumina, and cobalt-alumina catalysts were prepared by coprecipitated method. The surface area, crystal structure and pore volume of the catalysts were detected for various calcination temperatures, and the impact of activity and selectivity were compared on the dehydration reaction. The nickel-alumina and cobalt-alumina catalysts gave decreasing surface area with increasing calcination temperatures. However, the pore volume was independent from the calcination temperature. The crystalline properties were determined by x-ray diffraction. The results showed that cobalt-alumina catalyst had trace molecules (Co_3O_3 and Co_3O_4) and the scale of the crystals size were from 7 to 23 nm depending on the increasing calcination temperature. On the other hand, the nickel-alumina catalyst had uniform crystal phase, and the scale of the crystal size was from 2.5 to 9.5 nm respectively increasing calcination temperature. The selectivities of alumina and cobalt-alumina were close to 100% for dehydration process. Whereas the selectivity of nickel-alumina was 65% due to occurring dehydrogenation reaction and the selectivity could be increased with increasing calcination temperature. The experiments proved that increasing reaction temperature decreasing olefin product (2-octene) instead of ether. The octahedral and tetrahedral sites were decided to take similar role for product selectivity. Even though, the catalysts gave good results, the active sites of alumina were not improved by supporting cobalt and nickel for dehydration reaction [36].

Kang et al. presented an investigation about dehydration reaction of various alcohols which were ethanol, 1- propanol, 2-propanol, and isobutanol over γ-Al_2O_3 catalyst. They investigated the effect of chain length of the alcohol, selectivity, and water impact. The dehydration products were mentioned ethers and olefins. The experimental results proved that the existence of water prevented dehydration reaction and blocked active sites on the catalyst. Additionally, the effect of pyridine addition was evaluated on dehydration reactions. The pyridine addition was observed with poisoning effect on catalyst, it leaded to decrease Lewis acid sites where the reaction proceeds. The kinetic mechanism of the reaction showed that the cleavage of O-H bond did not have an impact on olefin formation, and the necessary step was determined that the breakage of C−O and C−H bonds to form olefins. On the other hand, the cleavage of C-O and Al-O bonds were given as a rate determining step for ether formation. According to experiments, the secondary alcohol (2-propanol) gave the highest olefin selectivity. Furthermore, the researchers mentioned that increasing carbon chain of the alcohols leads to increase olefin formation [37].

Ellis et al. tried to explain dehydration and dehydrogenation reactions by utilizing 1-butanol over metal oxide catalysts (γ-Al_2O_3, CeO_2, CuO, Fe_2O_3, MgO, rutile-TiO_2 (TiO_2-R), anatase-TiO_2 ((TiO_2-A), SnO_2, V_2O_5, WO_3, ZrO_2, and ZnO) which were modified with phosphonic acid. The investigation was understanding phosphonic acid (methylphosphonic acid (MPA) and octadecylphosphonic acid (ODPA)) monolayers effect on activity and selectivity of the catalysts. This modification presented that dehydrogenation and condensation reactions were decreased, but it did not clarify dehydration reaction. The electronic polarizability of oxygen atom was found to assist dehydration reaction. The TiO_2-A, CeO_2 and SnO_2 catalysts were defined the best choices for dehydration activity, although γ-Al_2O_3 was observed giving an improvement for selectivity of dehydration reaction beside of TiO_2-A, CeO_2 and SnO_2 (Figure 14 and Figure 15) [38].

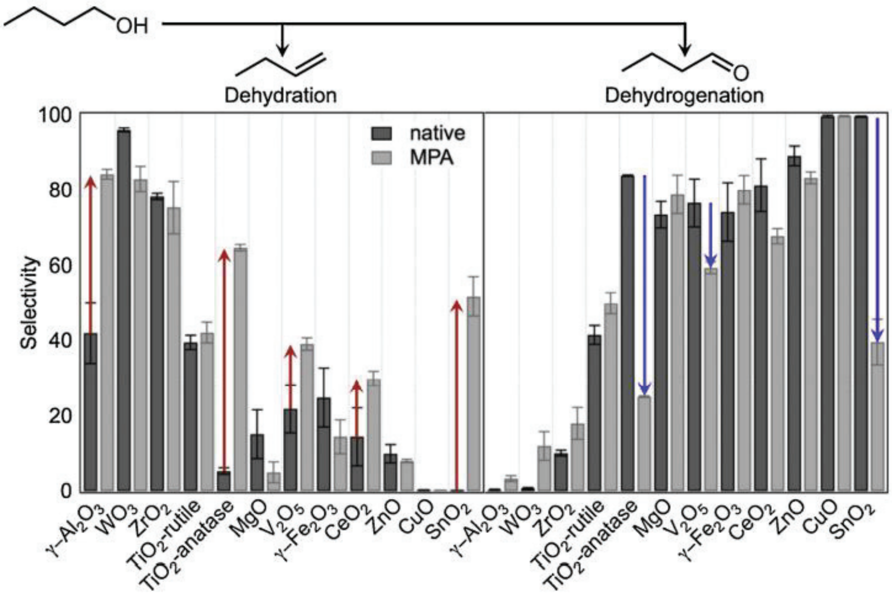

Figure 14. Dehydration and dehydrogenation reactions for 1-butanol and the catalysts selectivities on products at 250 °C [38].

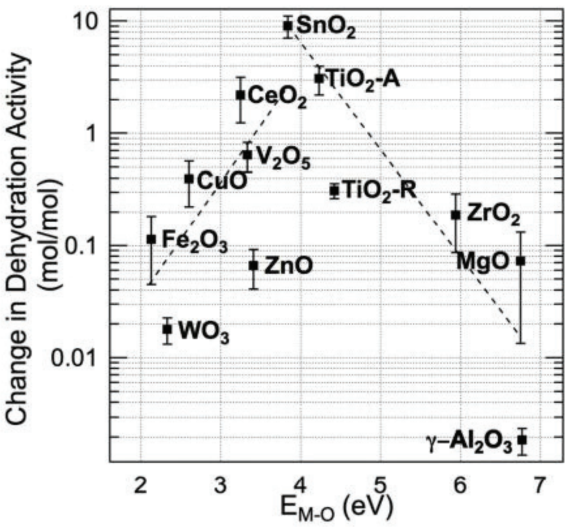

Figure 15. Dehydration activities after MPA modification versus metal-oxygen bond strength [38].

Shinohara et al. examined four kinds of metal oxides which were Al_2O_3, SiO_2, ZnO and CdO for determination of dehydration and dehydrogenation mechanisms by utilizing 2-propanol. Furthermore, they used Molecular Orbital Package (MOPAC) for theoretical experiments to explain molecular mechanisms. In Figure 16, the theoretical structure models presented that the extraction of H_β was the rate determining step for dehydration process. The β-hydrogen extraction was optimized with distance of oxygen (a) of the alcohol, metal acid site (b) and surface of the oxygen (c) due to basic site effect. For dehydration reaction, the strength and length of C_α-O bonds were determined having important role because of its oxygen which could interact with an electrophile such as hydrogen (Figure 16 (2)). Furthermore, the researchers mentioned that if the metal-oxygen bond is stronger than C_α-O bonds, the reaction mechanism runs on dehydration reaction. Whereas the activity energies were evaluated. The activity energies of acidic metal oxide catalysts (SiO_2 and Al_2O_3) were smaller than basic oxide catalysts (ZnO and CdO) for alcohol dehydration. The selectivities of the metal oxide catalysts were investigated. Hence, while ZnO and CdO were selective for dehydrogenation reaction, the dehydration reaction was dominant for SiO_2 and Al_2O_3 (Table 9). Hereby, the cleavage of C_α-O bonds was described as rate determining step. Besides all, the primary (methanol, ethanol, n-propanol, n-butanol), secondary (s-butanol, 2-propanol) and tertiary (t-butanol) alcohols were investigated that desorption of their alkoxy groups on SiO_2. The activation energies of the alkoxy groups decreased in order primary, secondary and tertiary respectively. According to this study, the lowest required activation energy was the most possible reaction, so the dehydration rate decreased tertiary, secondary and primary alcohols respectively. The researchers made this evaluation by applying experimental research in gaseous phase and they explained the dehydration mechanism depended on the cleavage of C_α-O bonds while dehydrogenation mechanism proceeded α-hydrogen which extracted from alkoxy group [39].

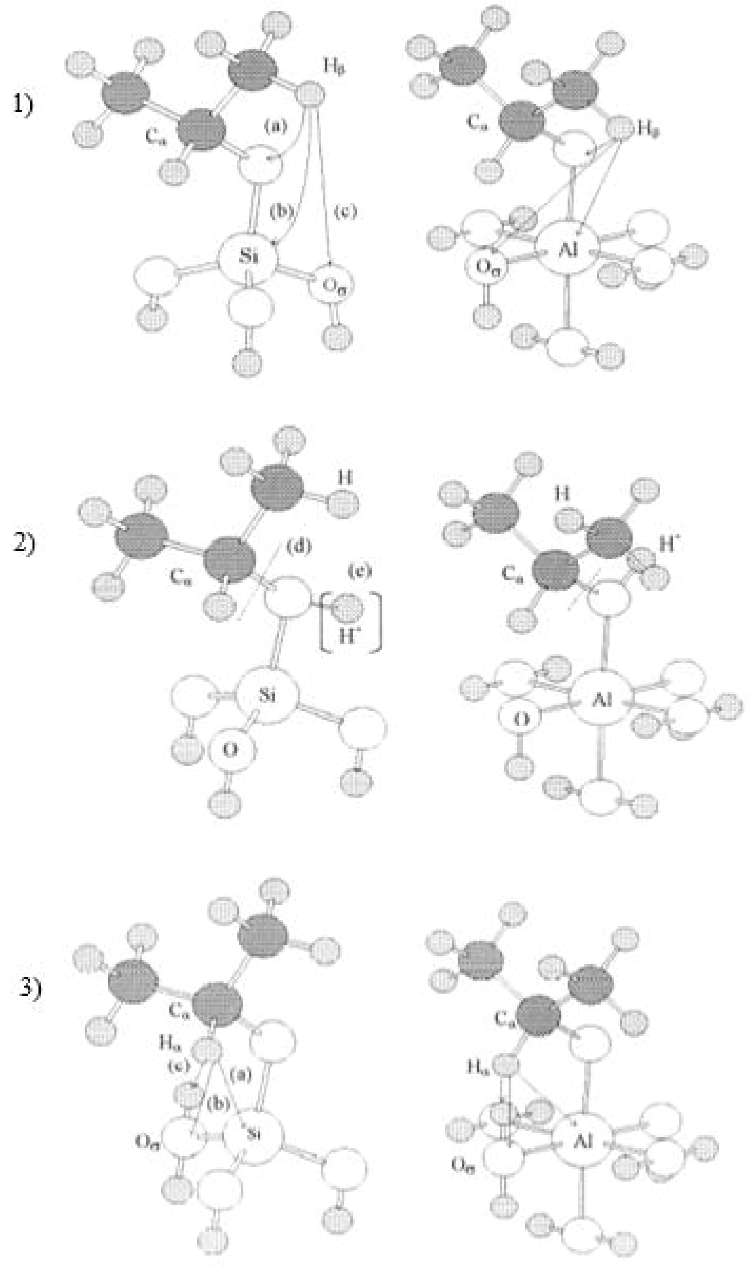

Figure 16. Molecular mechanisms of dehydration and dehydrogenation reactions of 2-propanol over metal oxide catalysts (SiO_2 and Al_2O_3), 1) dehydration mechanism on extraction of H_β, 2) dehydration mechanism according to C_α-O bonds 3) dehydrogenation mechanism [39].

Table 9. Selectivities of the metal oxide catalysts on dehydration and dehydrogenation processes by using 2-propanol [39].

Oxides	Dehydration (%)	Dehydrogenation (%)
Al_2O_3	100.0	0.0
SiO_2	95.6	5.0
CdO	5.6	94.4
ZnO	2.2	97.8

Generally, alumina is cheap and robustness material. Therefore, the whole previous works mentioned alumina-based catalyst have a potential for a selective, active, and effective catalyst on dehydration reaction with an improvement of its properties.

2.2. Comparison of The Catalysts

Most of the catalytic reactions take place on metallic samples. The metals are desired due to laborless preparation and characterization of the materials. Dehydration reaction runs on acidic sites which are Lewis and Brønsted sites. During the reaction, appropriate water molecule always exists, and it generates Brønsted sites where side reactions proceed. The distribution of acidic sites is important to investigate the characteristic of acidic materials. Furthermore, the surface sites and crystalline size impacts selectivity of the reaction [11]. In previous researchers, ion exchange resins, zeolites and solid metal oxide catalysts were mostly favoured for this process.

The ion exchange resins, which based on anion and cation exchanges, were observed with good efficiency, selectivity and activity for dehydration process. Whereas, they presented leaching problem in the reaction, and the existence of water showed inhibition impact on the resins even the result of the application of water removal system [30-32, 40, 41].

Zeolites have been defined as crystalline with well-defined structures. Also, they are mentioned that they provide high activity, chemical resistance and thermal stability, also the zeolites are known as shape and size selective catalysts. Thus, it has restrictions for product distribution, and it controls the reaction. When the small particle size of zeolite leads to decreasing shape selectivity, it assists to increasing surface area. Moreover, the lifetime of zeolite depends on coke deposition which can be side products such as long chain, ring and etc. Recently, bifunctional catalyst ZSM-5 took attention for dehydration process. Even though ZSM-5 was observed with good yield, high selectivity and thermal stability, the pores of ZSM-5 prevented high chain intermediates. Also, in ZSM-5, increasing Si/Al ratio leaded to proceed the reaction on Brønsted acid sites. [4, 11-13, 42]. Furthermore, the water molecules were defined as problem for the zeolite because of decreasing acid sites on surface and pore opening. Besides the silica/alumina ratio effect on acidity, the increasing of Brønsted acid sites and the decreasing of acidity were observed by water. Thus, the ZSM-5 was situated selective for side reactions such as dehydrogenation instead of dehydration [43, 44].

The solid metal oxide catalysts were investigated, and alumina catalyst was generally desired for the dehydration reaction due to low cost, high surface area, porosity and other tailor-made characteristic properties [1]. Phase of alumina (γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3 and α-Al_2O_3), which transform with calcination temperature, was found having impact of dehydration process. γ-Al_2O_3 was mesoporous catalyst with high surface area, so its structure assisted to reduce internal and external mass transfer limitations and tended to produce olefins [45, 46]. Alumina catalysts were mentioned that being weakly acidic catalysts, and silica addition made it more acidic and stable bifunctional catalyst. The silanol groups of silica supported to prevent poisoning of the catalyst from the water. Whereas the Al-OH groups of alumina was observed providing Lewis acid sites where dehydration reaction proceeds and increasing silica amount leaded to decreasing the Al-OH groups and increasing Brønsted acid sites [4, 47].

To sum up, the whole types of catalysts were presented with their characteristic properties for dehydration process. Ion exchange resins and zeolites had good properties, but they needed moderately improvements to obstruct water inhibition. The silica-alumina metal oxide catalyst promised well advanced characteristic property for elimination of water from the catalyst surface. Thus, the synthesis of silica-alumina catalyst will be more reasonable approach for alcohol dehydration.

CHAPTER 3

MATERIALS AND METHOD

3.1. Materials

In this study, Al_2O_3- SiO_2 was synthesized as a solid mixed oxide catalyst using sol-gel method. The compositions of Al_2O_3-SiO_2 were 25/75, 50/50 and 75/25 with application of various calcination temperatures such as 500℃, 700℃ and 900℃.

In the synthesized of the catalyst, tetraethyl orthosilicate (TEOS) was the initiator for silica, and aluminium isopropoxide (AIP) was starter for alumina. Ethanol (EtOH) and deionized water (DIW) were used as solvents, and hydrochloric acid (HCl) and nitric acid (HNO_3) were used as peptizing agent in the sol-gel method. For synthesized of the metal oxide catalyst, the properties of the used chemicals were given in Table 10.

Table 10. Properties of the used chemicals for synthesized of the metal oxide catalyst.

Materials	Chemical Formula	Molecular Weight (g/mol)	Density (g/ml)	Purity (%)
AIP	$Al(OCH(CH_3)_2)_3$	204.24	1.035	98
TEOS	$Si(OC_2H_5)_4$	208.33	0.935	98
Nitric Acid	HNO_3	63.01	1.4	70
DIW	H_2O	18.02	1	100
Hydrochloric Acid	HCl	36.45	1.16	36.5
EtOH	C_2H_5OH	46.07	0.79	99.5

3.2. Methods

In this study, experiments can be categorized into four groups: catalyst preparation, catalyst characterization, Al_2O_3-SiO_2 catalyst testing for 1-octanol dehydration reaction and product characterization.

3.2.1. Catalyst Preparation

The Al_2O_3-SiO_2 was synthesized by sol-gel method which is improved by the research group of Prof. Dr. Erol Şeker. Firstly, silica sol was started to preparation. The necessary amount of TEOS and EtOH were mixed for 30 minutes at 85℃. Then, the necessary amount of HCl and DIW were added to that mixture, and the solution was mixed for 2 hours at 85℃. During the silica solution were mixing, the preparation of alumina sol was started. AIP and DIW were mixed for 1 hour at 85℃ on another heat stirrer. Nitric acid was added to that mix for 20 minutes at 85℃. When the proper time ended for silica sol, it was added to alumina sol. And they mixed for 1 hour at 85℃. After that, the final silica-alumina sol was waited to get gel form under 60℃ for 1 hour without stirring. Then, the silica-alumina gel was dried for 6 hours at 120℃. Three silica-alumina gels were prepared with the same procedure according to weight percentages such as 25/75, 50/50 and 75/25. The calcination time (6 hours) was the same for the whole synthesized catalysts, but the calcination temperature was applied as 500℃, 700℃ and 900℃. The synthesized catalysts were grinded under 30 μm getting appropriate powders for application of the reaction.

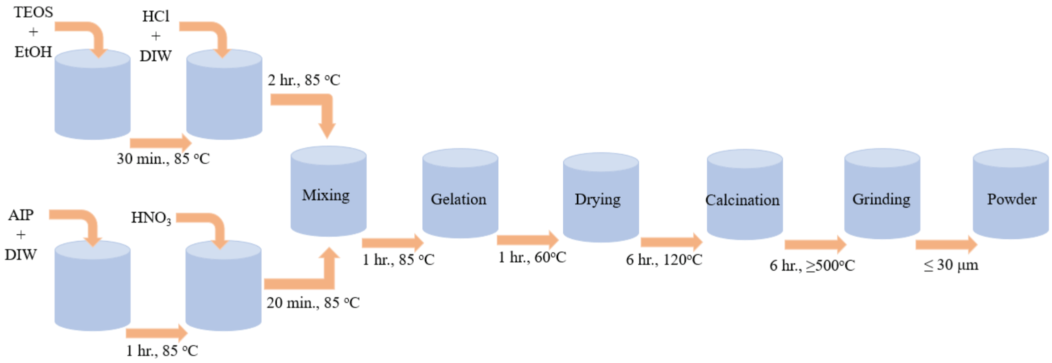

Figure 17. Experimental procedure for the synthesized Al_2O_3-SiO_2 catalysts.

3.2.2. Catalyst characterization

The characteristic and physicochemical properties of the synthesized catalysts were identified with applying temperature programmed desorption (NH_3-TPD and CO_2-TPD) analysis.

3.2.2.1. NH_3-Temperature Programmed Desorption (TPD)

To describe acidic properties such as acidic strength and acid amount, temperature programmed desorption of the basic molecule such as ammonia is generally used, and it calls NH_3-TPD. The identification of exact location of Brønsted acidic sites and Lewis acidic sites is not easy to understand. The acidity means the number of acidic sites on solid catalyst. The acidic strength depends on the base adsorption tendency of catalyst [4].

For NH_3-TPD analysis, Shimadzu GC-17A gas chromatograph equipped with a TCD detector and an external oven were used to carry out TPD analysis. First catalysts are activated by heating up to 500 ºC with 10 ºC, 30 minutes ramp and kept at that temperature for 1 h and cooled to 50 ºC with 15 cm^3/min. ramp under helium flow, which is carrier gas, to prepare catalysts surface for TPD characterization. Then gas flow changes and waited for 1h with 30 cm^3/min. NH_3 over 100 mg catalyst. Then gas low changes again by adding helium, and adsorption takes places by increasing temperature up to 500 ºC with 70 cm^3/min. After those catalysts are cooled down to 50 ºC with 15 ºC/min. The program stops recording, so detected NH_3 peaks are calculated by TCD responses of known amounts of NH_3 gas for quantitative measurements.

3.2.2.2. CO_2-Temperature Programmed Desorption (TPD)

To describe basic properties such as basic strength and basic amount, temperature programmed desorption of the acidic molecule such as carbon dioxide is generally used, and it calls CO_2-TPD. The basic property can be described as tendency of donation an electron pair to an adsorbed acid [4].

For CO_2-TPD analysis Shimadzu GC-17A gas chromatograph equipped with a TCD detector and an external oven were used to carry out TPD analysis. First catalysts are activated by heating up to 500 ºC with 10 ºC, 30 minutes ramp and kept at that temperature for 1 h and cooled to 60 ºC with 10 cm^3/min. ramp under helium flow, which is carrier gas, to prepare catalysts surface for TPD characterization. Then gas flow changes and waited for 1h with 30 cm^3/min. CO_2 over 100 mg catalyst. Then gas low changes again by adding helium, and adsorption takes places by increasing temperature up to 500 ºC with 70 cm^3/min. After those catalysts are cooled down to 60 ºC with 10 ºC/min. The program stops recording, so CO_2 peaks of the analysis are calculated by TCD responses of known amounts of CO_2 gas for quantitative measurements.

3.2.3. Al_2O_3-SiO_2 Catalyst Testing for 1-Octanol Dehydration Reaction

The experimental system proceeded in liquid phase. Batch system was settled up with condenser engine to eliminate losses in gaseous phase (Figure 18). The synthesized catalyst (0.2 g) and 1-octanol (1 g) were put into an erlenmeyer with magnetic stirrer, and also oil was utilized instead of water in the beaker, whose inside also the erlenmeyer exists, because of experimental parameters. The reaction proceeded at 150℃ and the reaction time was mainly 4 h. Then, the mixture put in centrifuge (Hettich Rotina 38) to separate catalyst and the products at 15000 rpm for 8 minutes.

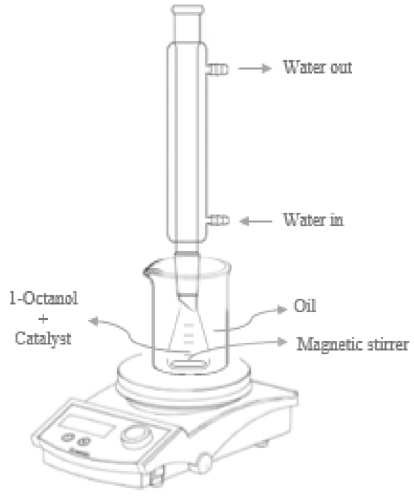

Figure 18. The designed system of the experiments for the alcohol dehydration in liquid phase.

3.2.4. Product Characterization

Gas chromatography (GC) technique is a helpful tool to determine concentrations and amounts of the compounds in a sample. A usual GC engine consists of three main parts that are capillary or open-tubular column, carrier gas and stationary phase. There is a general scheme about GC analysis in Figure 19 [48].

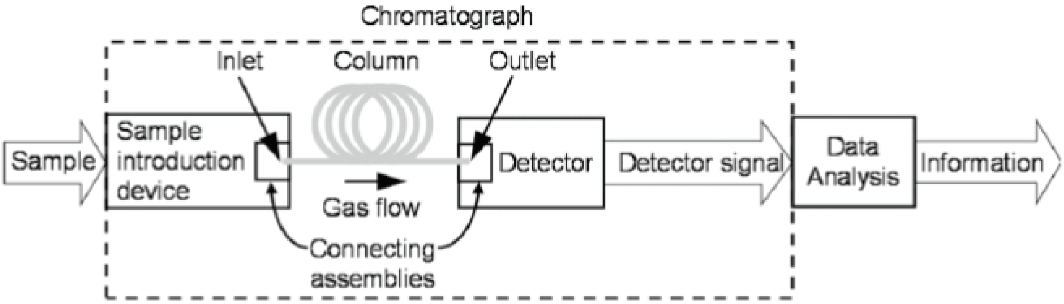

Figure 19. A general diagram for gas chromatography system [48].

Furthermore, every analysis needs a particular method whose parameters are specified for that analysis to separate compounds. The concentration of the sample and validation of the method mainly affects the separation of the peaks which is helpful to clarify number of components and their existence amount in the sample. The concentration of the sample in solute, flow rate, heating rate, and column separation performance, analysis time, and detection of the peaks are main parameters to find optimal working conditions [48].

In the experimental product analysis Gas Chromatography-Mass Spectrometer **(**GC-MS) (Agilent 6890N / 5973N) was utilized to identify compounds and their existence amounts in the liquid mixture. The applied method was determined by the specialists of the Environmental Development Application and Research Center, and the determination of compounds and their existence amount were done by Handan Gaygısız.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Determination of Maximum Conversion and Error Calculation for 1-Octanol Dehydration over Al_2O_3-SiO_2 Catalysts

In this study, GC-MS analysis utilized to identify products and their existence amounts according to their areas. Furthermore, this analysis presented conversion of 1-octanol according to difference of 1-octanol areas (initial and final). In Figure 20, the results of GC-MS analysis showed that the maximum conversion was obtained by application of 50%Al_2O_3-50%SiO_2 (700℃).

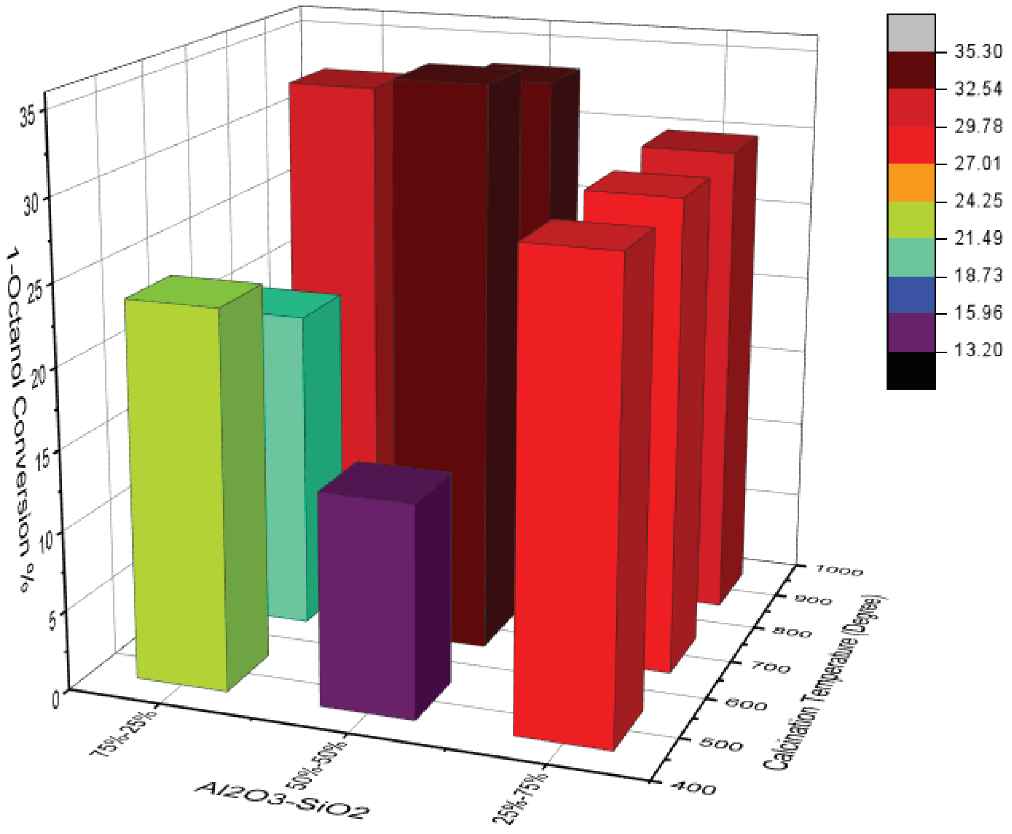

Figure 20. 1-Octanol conversion percentage values depending on the Al_2O_3-SiO_2 ratio and their calcination temperatures.

Thus, the repeat experiments run on 50%Al_2O_3-50%SiO_2 (700℃) to determine error value whose reason could be human mistake, difference the injection concentration to the engine etc. The one sample t-test applied to find percentage error for the experiments by utilizing the results of the repeat experiments (Table 11).

Table 11. One Sample t-Test on The Results of The Repeat Experiments.

One-Sample t-Test: 50%Al_2O_3- 50%SiO_2 (700℃)

Variable	N	Mean	StDev	SE Mean	95% CI
50%Al_2O_3- 50%SiO_2 (700℃)	6	33,75	4,95	2,02	(28,56; 38,95)

The percentage error of the experiments calculated as 15.4% due to one sample t-test. This calculated error applied conversion bars in Figure 21. The results showed that 50%Al_2O_3-50%SiO_2 (500℃) gave the smallest conversion, and 75%Al_2O_3-25%SiO_2 (700℃) gave inadequate conversion for the experiments. Moreover, 25%Al_2O_3-75%SiO_2 presented stable behavior for its whole calcination temperatures. Besides that, 50%Al_2O_3-50%SiO_2 demonstrated relatively high conversion at 700℃ and 900℃ calcination temperatures, while 75%Al_2O_3-25%SiO_2 indicated at only 900℃ calcination temperature.

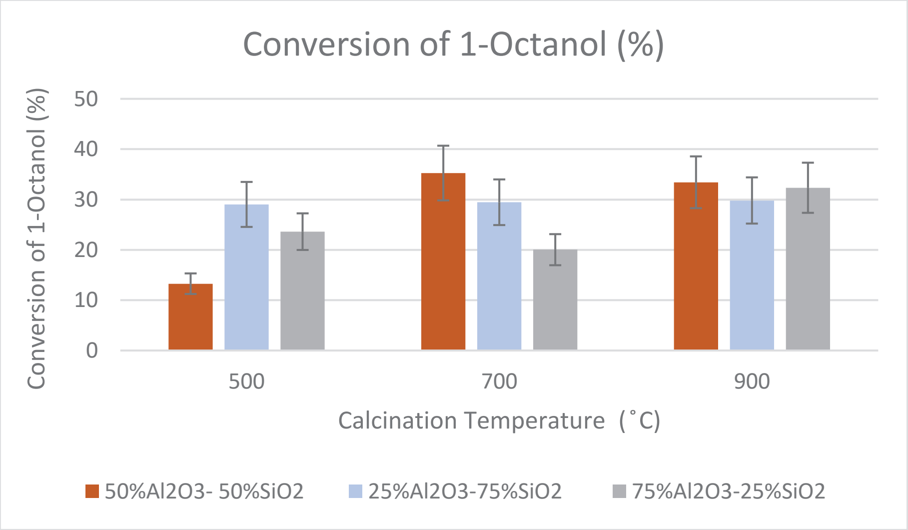

Figure 21. Conversion of 1-Octanol over Al_2O_3-SiO_2 catalysts.

4.2. Product Distribution of 1-Octanol Dehydration over Al_2O_3-SiO_2 Catalysts

The whole synthesized products were tested in GC-MS at liquid phase. The area percentages of the products gave some knowledge about their existence relationship in the total area of the sample. Furthermore, it assisted to clarify the characteristic properties of applied catalysts. Octane, 1,4-epoxy, octyl ether, octanal, formic acid octyl ester, acetic acid octyl ester, heptanoic acid octyl ester and oxalic acid 2-ethylhexyl tetradecyl ester (possible product) were determined as the main products. Therefore, the percentage distribution of the main products can be seen in Figure 22.

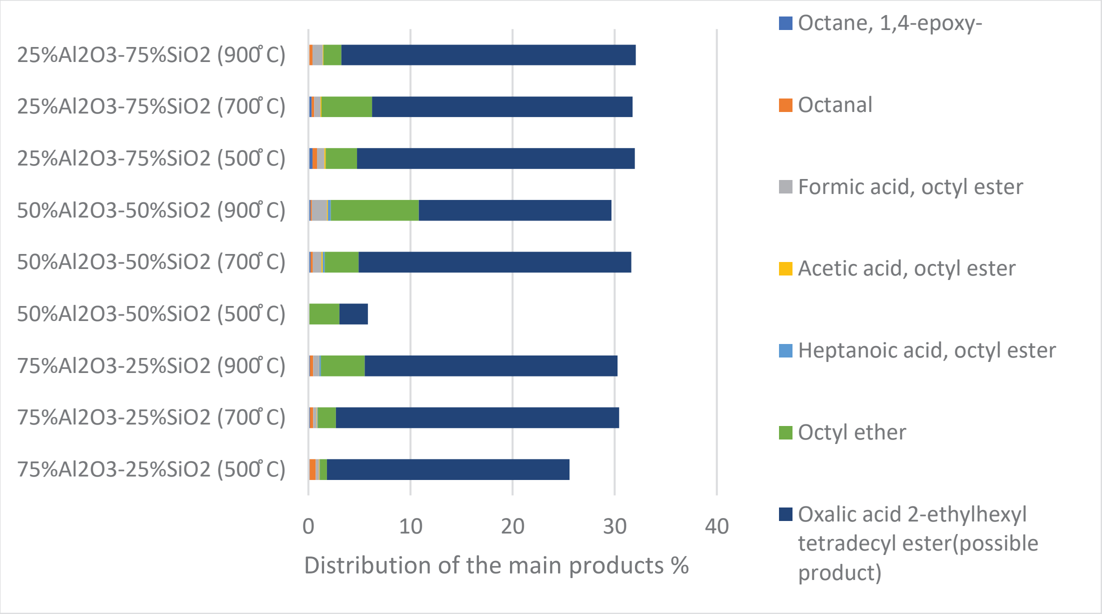

Figure 22.The percentage distribution of the main products over synthesized catalysts according to GC-MS data.

Octanal ($C_8H_{16}O$) and Octane 1,4-epoxy ($C_8H_{16}O$) were observed with small amounts, and the appearance of octane 1,4-epoxy ($C_8H_{16}O$) could be ignorable. They both could be produced by oxidation and dehydrogenation reactions. According to GC-MS data, the percentage of octanal conversion over synthesized catalysts were presented in Figure 23. Even though, octanal conversion was small, the maximum conversion was observed by usage of 75%Al_2O_3-25%SiO_2 (500℃). Whereas the smallest conversion of octanal was seen by utilizing 50%Al_2O_3-50%SiO_2 (500℃).

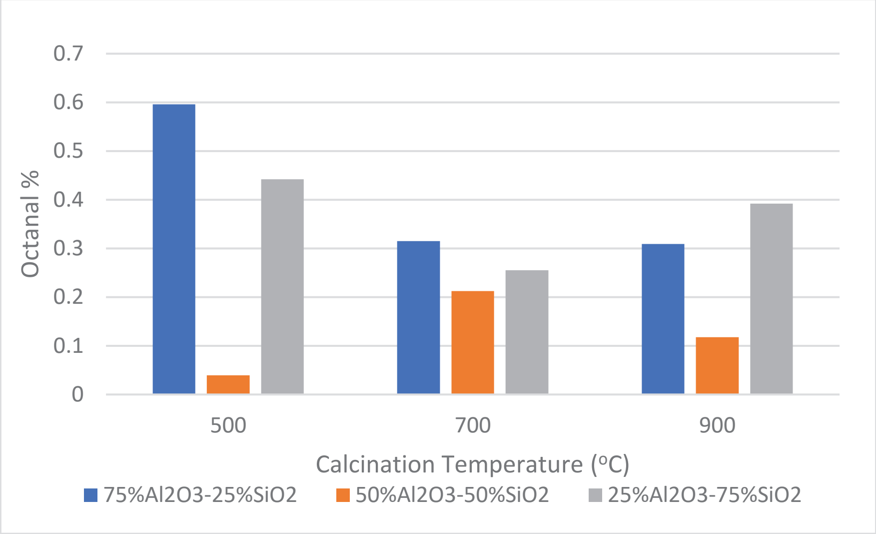

Figure 23.The percentage of octanal conversion over synthesized catalysts based on GC-MS data.

The octyl ester products could be synthesized the following route of oxidation and dehydration, respectively. The conversion percentage of these products was smallest over 75%Al_2O_3-25%SiO_2 at any calcination temperature. Although the existence of these products was not predicted at 500℃ calcination temperature for 50%Al_2O_3-50%SiO_2. The highest conversion percentage was observed for 50%Al_2O_3-50%SiO_2 at 700℃ and 900℃ calcination temperatures (Figure 24).

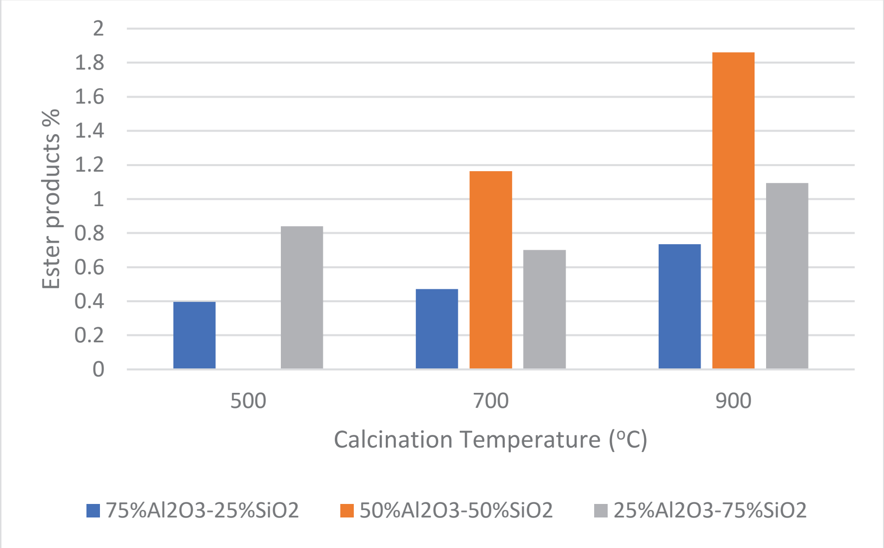

Figure 24. The percentage of total ester products conversion (Formic acid, octyl ester, Acetic acid, octyl ester and Heptanoic acid, octyl ester) over synthesized catalysts based on GC-MS data.

Octyl ether synthesized reaction was bimolecular dehydration, and the percentage of its conversion over synthesized catalysts was shown in Figure 25. The highest conversion belonged to 50%Al_2O_3-50%SiO_2 (900℃). The increasing conversion behaviour was seen for 75%Al_2O_3-25%SiO_2 and 50%Al_2O_3-50%SiO_2 catalysts with increasing calcination temperatures. Besides, 75%Al_2O_3-25%SiO_2 (500℃ and 700℃) and 25%Al_2O_3-75%SiO_2 (900℃) catalysts showed the small octyl ether conversion.

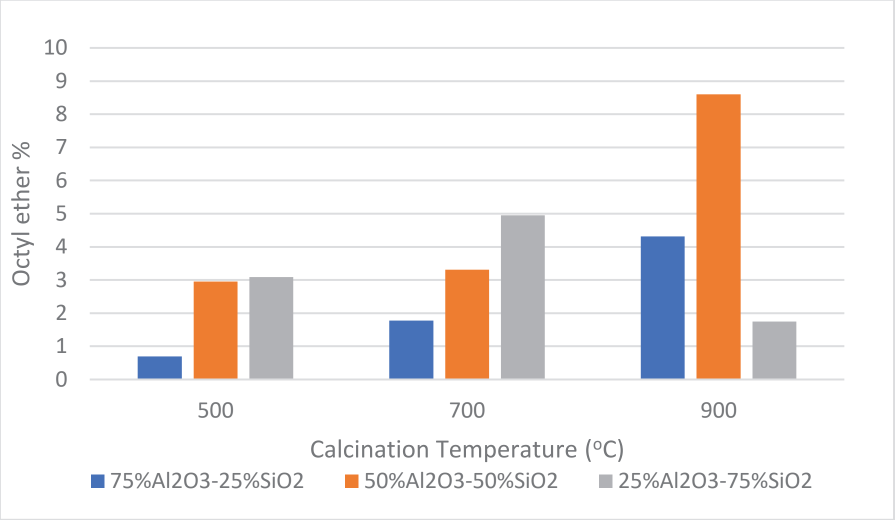

Figure 25.The percentage of octyl ether conversion over synthesized catalysts based on GC-MS data.

For application of all catalysts, the highest conversion belonged to oxalic acid 2-ethylhexyl tetradecyl ester (possible product). The clarification of its synthesis reaction was uncertain, and it gave weak match for any product according to GC-MS results. Furthermore, the percentage of oxalic acid 2-ethylhexyl tetradecyl ester (possible product) conversion was extremely high for all synthesized catalysts, except for 50%Al_2O_3-50%SiO_2 (500℃) (Figure 26).

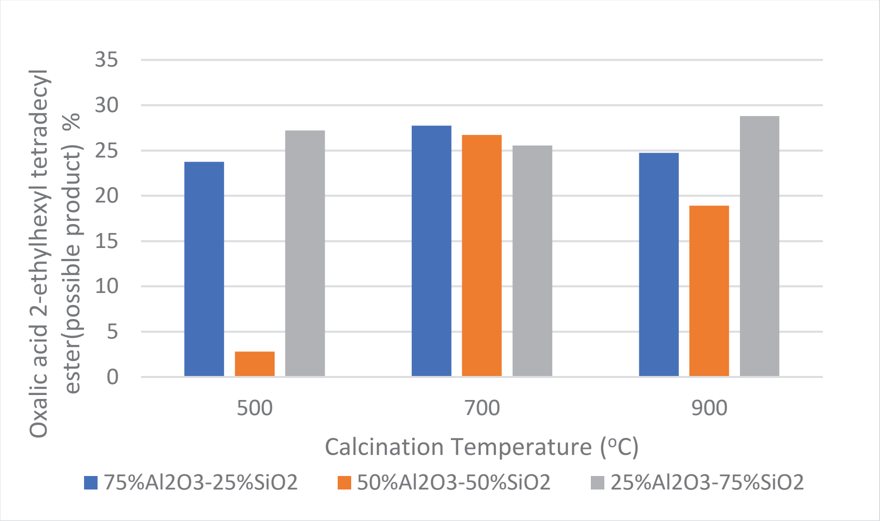

Figure 26.The percentage of oxalic acid 2-ethylhexyl tetradecyl ester (possible product) conversion over synthesized catalysts based on GC-MS data.

The main product of dehydration reaction is olefins in literature. In the experiments, there was not observed any olefin in liquid phase because of the experimental conditions (4h, 150℃). The boiling point of 1-octene was 121℃ and 2-octene was 125℃, so the olefins vaporized. When the gas phase was analysed, the main products were 1-octene, 2-octene and octanal. The GC-MS was not suitable for gas phase analysis, and the conversion calculation could not do for gas phase due to losing gas mixture.

4.3. Reactions and Their Pathways

The dehydration reaction was aimed, and it is known that the main product was olefins and side product was ether, which was synthesized by bimolecular dehydration reaction, except of water. Despite that the experiments showed that there was not only dehydration reaction, and wide range product scale was obtained by dehydration, oxidation, dehydrogenation, hydration, hydrogenation, bimolecular dehydration, and hydrolysis reactions (Figure 31).

Dehydration reaction requires an acidic catalyst to remove hydroxyl group, and generally yields Saytzeff products. These products follow Saytzeff rule that means the most exist one is the dominant one [5]. Thus, sometimes, secondary carbon is carbocated instead of hydroxyl group bonded carbon on the 1-octanol. In this case, 2-octene is formed during 1-octanol dehydration reaction (Figure 32). If the olefin formation aimed, side products should be removed as they formed to prevent reverse reaction (Figure 33) and side reactions.

In the experiments, batch system used. Thus, whole products and the radicals were in the same place. It caused multiple side reactions. Also, besides the batch system effect, using a primary alcohol for dehydration process leaded to low alkene yield, and these alkenes were observed only in gas phase. Furthermore, the highest formation of oxalic acid 2-ethylhexyl tetradecyl ester was observed and was called as possible product. The reason was the big chain ester production was possible, but it had poor match with that name according to GC-MS results.

On the other hand, hydrogenation of olefins gives alkanes (octane). Dehydrogenation, oxidation, oxidative hydrogenation reactions give hydrogen atoms and olefins tends to accept hydrogen to break their weak bond to be more stable [5].

Bimolecular dehydration produces ethers with high yield from primary alcohols. If the alcohol is secondary or tertiary, an alkene result. The reaction proceeds over acidic side of the catalysts. Ether lack of the hydroxyl group of the alcohols, so they are less reactive and less likely to participate in unwanted side reactions [5]. During the experiments, two molecule 1-octanol reacted with themselves and produced octyl ether by bimolecular dehydration reaction (Figure 34).

Dehydrogenation of alcohol proceed on basic site of the catalyst. For the 1-octanol usage, hydrogens leaved the alcohol and weakly bonded to basic site on the surface of the catalyst and leads to dehydrogenation [4]. The dehydrogenation products were octane, 1,4-epoxy and octanal. The oxygen leaded oxidation reaction, so aldehydes and water were produced with this reaction. Moreover, the further oxidation of aldehydes produced carboxylic acid [22]. These carboxylic acids reacted with 1-octanol and leaded to form ester products, this type of reactions called as Fischer esterification [5].

4.4. Characterization of Al_2O_3-SiO_2

It is well known fact that dehydration reaction requires acidic catalyst, and Al_2O_3-SiO_2 catalysts are bifunctional catalysts which presents acidic and basic properties [4]. The product distribution and occurred reactions gave a clue about that. Thus, to determine acidic and basic effects of the catalysts, NH_3-TPD and CO_2-TPD results and the characteristics of Al_2O_3-SiO_2 catalysts presented in this section.

4.4.1. Determination of Acidity and Acidic Strength over The Catalysts

The Al_2O_3-SiO_2 catalysts are mixed oxide solid catalysts which includes Lewis acid sites and Brønsted acid sites. Even though the dehydration reaction proceeds on Lewis acid sites according to literature, the separately identification of these acid sites is almost impossible [4]. Thus, the definitions of acidity made for total acid sites, and the acidic strength included both acid sites.

The NH_3-TPD results were used to determine acidity and acidic strength. In Figure 27, signal versus time graph was prepared for all tested catalysts, the 50% Al_2O_3- 50% SiO_2 (700℃) catalyst gave the latest response. The reason could be characteristic properties of 50% Al_2O_3- 50% SiO_2 (700℃) catalyst. According to the NH_3-TPD data, the properties of tested catalysts were presented detailly in Table 12.

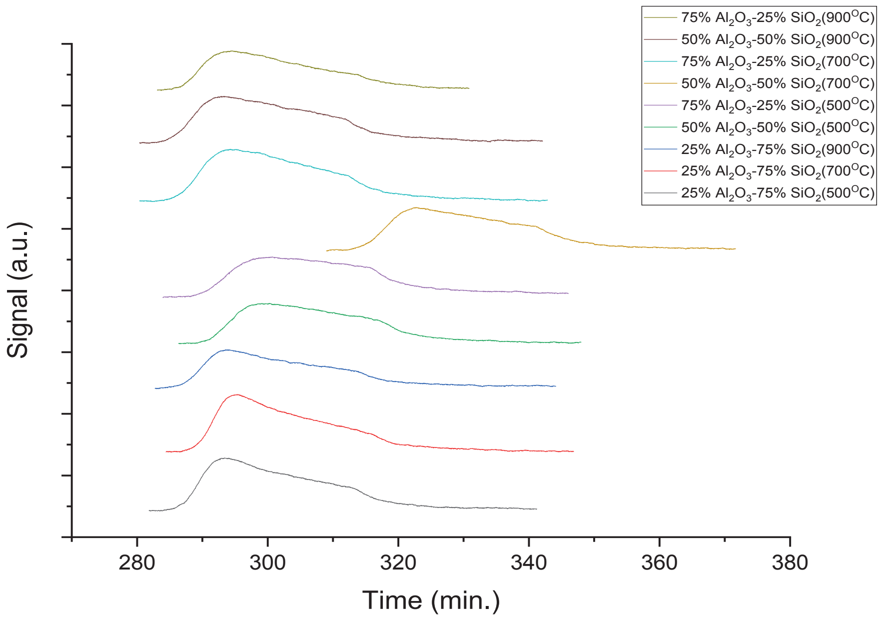

Figure 27. Signal versus time graph for all tested catalysts according to NH_3-TPD data.

Peak temperature shows the adsorption strength of NH_3 into catalysts, so it gives acidic strength of the catalyst. The peak temperature can be found by utilizing signal versus time graphs. The peak point can be chosen and be identified the specific time at that point from signal versus time graph, and the peak temperature can be found by using the specific time in temperature versus time graph. The Figure 28 was a graph for better understanding. Therefore, the acidic strength was the highest for 75%Al_2O_3-25%SiO_2 (500 °C) catalyst with

276.5 °C peak temperature (Table 12). Although 75%Al_2O_3-25%SiO_2 (500 ºC) catalyst had the highest peak temperature, it was still weak acidic catalyst due to being below 400 ºC [18]. Thus, all catalysts can be called as weak acidic catalysts.

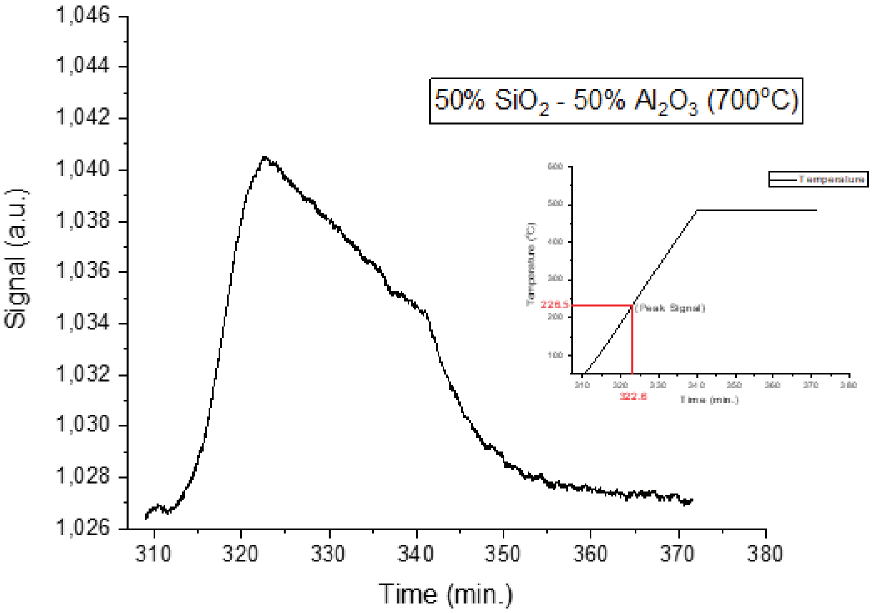

Figure 28. Signal versus time graph of NH_3-TPD for 50% Al_2O_3-50%SiO_2 (700 ºC).

The acidity of catalysts was found relatively higher than others 6.99 µmol/g, 6.78 µmol/g and 6.26 µmol/g for 25%Al_2O_3-75%SiO_2 (500 ºC), 50%Al_2O_3-50%SiO_2 (700 ºC) and 50%Al_2O_3-50%SiO_2 (500 ºC) catalysts, respectively. Whereas the acidity of 25%Al_2O_3-75%SiO_2 (900 ºC) catalyst was the lowest with 3.61 µmol/g. In Table 12, the acidity of catalysts can be seen for evaluation.

Table 12. Acidic properties of the synthesized Al_2O_3-SiO_2 catalysts by applied NH3-TPD.

Catalyst	T_{peak} (°C)	Acid amount based on NH3-TPD analysis				
		Area	Calibration factor (µmol NH3/area)	Total amount (µmol)	Sample mass (g)	Acidity of Catalyst (µmol/g)
25%Al_2O_3-75%SiO_2 (500 °C)	192.45	0.34	1.74	0.58	0.08	6.99
25%Al_2O_3-75%SiO_2 (700 °C)	181.61	0.35	1.74	0.61	0.11	5.55
25%Al_2O_3-75%SiO_2 (900 °C)	211.85	0.26	1.74	0.45	0.13	3.61
50%Al_2O_3-50%SiO_2 (500 °C)	216.85	0.30	1.74	0.52	0.08	6.26
50%Al_2O_3-50%SiO_2 (700 °C)	226.50	0.32	1.74	0.55	0.08	6.78
50%Al_2O_3-50%SiO_2 (900 °C)	210.00	0.33	1.74	0.58	0.10	5.51
75%Al_2O_3-25%SiO_2 (500 °C)	276.50	0.32	1.74	0.56	0.10	5.45
75%Al_2O_3-25%SiO_2 (700 °C)	226.83	0.36	1.74	0.62	0.11	5.86
75%Al_2O_3-25%SiO_2 (900 °C)	210.00	0.25	1.74	0.43	0.09	4.91

4.4.2. Determination of Basicity and Basic Strength over The Catalysts

In order to clarify basicity and basic strength of the Al_2O_3-SiO_2 catalysts, CO_2-TPD results utilized. In Figure 29, signal versus time graph was created for all tested catalyst presented with their CO_2 adsorption lines.

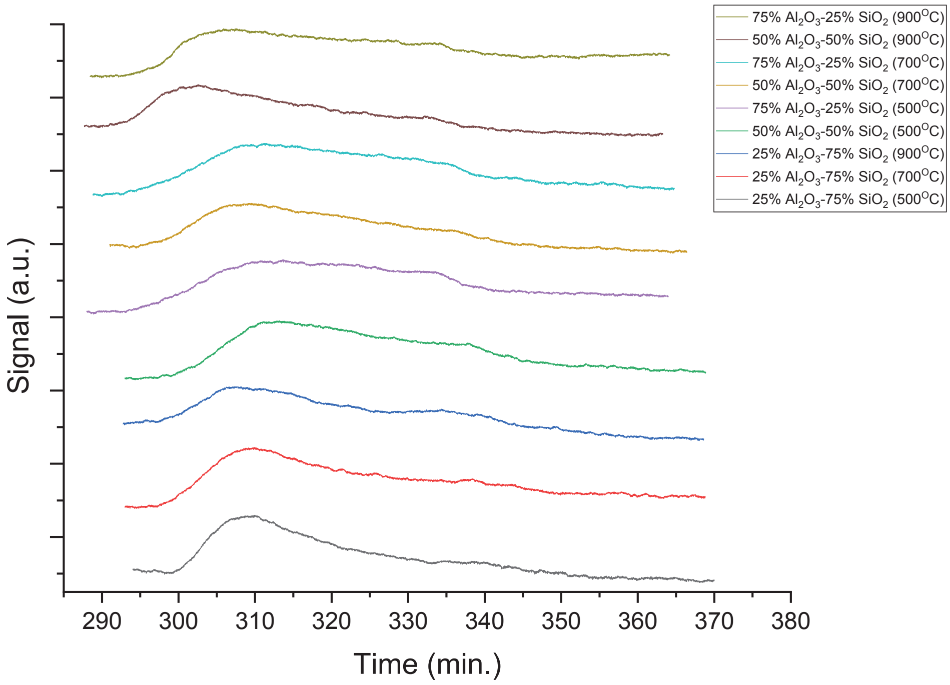

Figure 29. Signal versus time graph for all tested catalysts according to CO_2-TPD data.

The peak temperature of adsorbed CO_2 gives the strength of basic sites. The peak temperature can be found by utilizing signal versus time graphs. The applied route is same as NH_3-TPD graphs. The peak point can be chosen and be identified the specific time at that point from signal versus time graph, and the peak temperature can be found by using the specific time in temperature versus time graph. The Figure 30 was a graph for better understanding. The maximum basic strength belonged to 25%Al_2O_3-75%SiO_2 (500 ^{o}C) catalyst with 292.62 ^{o}C peak temperature. However, the whole catalysts were found having weak basic strengths in Table 13.

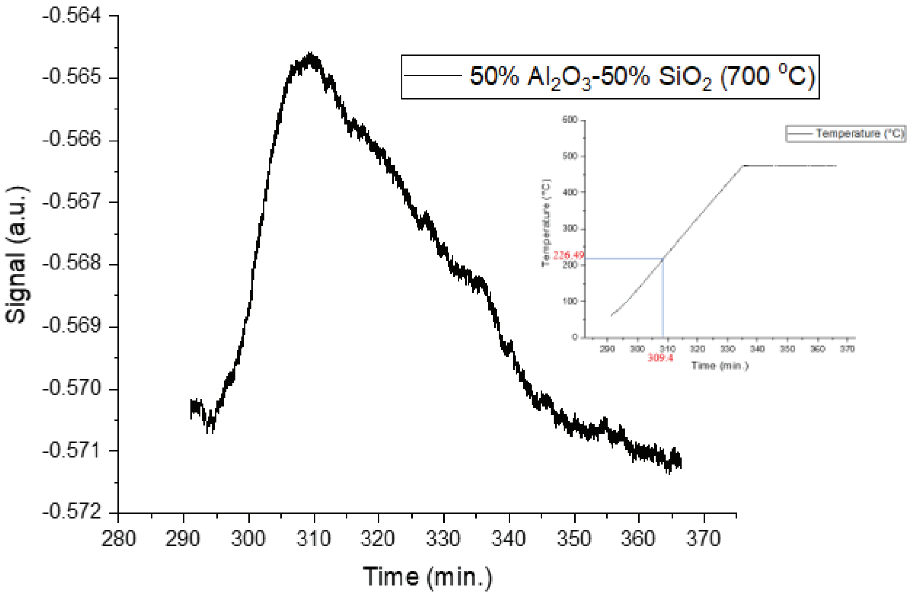

Figure 30.Signal versus time graph of CO_2-TPD for 50% Al_2O_3-50%SiO_2 (700 °C).

The basicity of catalysts was found relatively higher than others 178.77 µmol/g, 176.88 µmol/g and 172.24 µmol/g for 75%Al_2O_3-25%SiO_2 (500 °C), 50%Al_2O_3-50%SiO_2 (500 °C) and 25%Al_2O_3-75%SiO_2 (700 °C) catalysts, respectively. Whereas the basicity of 50%Al_2O_3-50%SiO_2 (900 °C) was the lowest with 108.31 µmol/g.

Table 13. Basic properties of the synthesized Al_2O_3-SiO_2 catalysts by applied CO_2-TPD.

Catalyst	T_{peak} (°C)	Basic amount based on CO_2-TPD analysis				
		Area	Calibration factor (µmol CO_2/area)	Total amount (µmol)	Sample mass (g)	Basicity of Catalyst (µmol/g)
25%Al_2O_3-75%SiO_2 (500 °C)	292.62	0.21	71.54	15.26	0.10	156.15
25%Al_2O_3-75%SiO_2 (700 °C)	258.36	0.23	71.54	16.35	0.09	172.24
25%Al_2O_3-75%SiO_2 (900 °C)	230.52	0.17	71.54	12.18	0.08	156.20
50%Al_2O_3-50%SiO_2 (500 °C)	234.10	0.24	71.54	17.28	0.10	176.88
50%Al_2O_3-50%SiO_2 (700 °C)	226.49	0.17	71.54	12.52	0.09	146.93
50%Al_2O_3-50%SiO_2 (900 °C)	186.73	0.14	71.54	10.05	0.09	108.31
75%Al_2O_3-25%SiO_2 (500 °C)	200.56	0.16	71.54	11.75	0.07	178.77
75%Al_2O_3-25%SiO_2 (700 °C)	211.56	0.21	71.54	15.06	0.10	154.45
75%Al_2O_3-25%SiO_2 (900 °C)	186.32	0.16	71.54	11.62	0.10	115.63

CHAPTER 5

CONCLUSION

In this study, the effect of acidic and basic properties of solid catalysts were investigated on dehydration reaction of 1-octanol over alumina-silica metal oxide catalysts.

The alumina-silica catalysts were prepared by sol-gel method with 25-75, 50-50 and 75-25 molar ratios, and the calcination temperatures were 500℃, 700℃ and 900℃ for 6 hours. The NH_3-TPD, CO_2-TPD analysis were utilized to determine characteristic properties of synthesized catalysts. Therefore, the reactions proceeded at 150℃, 4 hours on batch reactor system. The product mixtures were analysed by GC-MS for identification of components and calculation of 1-octanol conversion.

The major outcome of this study shows that:

- The main products were octanal, ester products, octyl ether and oxalic acid 2-ethylhexyl tetradecyl ester (possible product) for all synthesized Al_2O_3-SiO_2 catalysts. The maximum 1-octanol conversion (35.26%) was observed over 50%Al_2O_3-50%SiO_2 (700℃) catalyst.
- The small amount of octanal which was less than 0.6% and large amount of oxalic acid 2-ethylhexyl tetradecyl ester (possible product) which was more than 18% for all catalysts, except 50%Al_2O_3-50%SiO_2 (500℃) catalyst. The product distribution of 50%Al_2O_3-50%SiO_2 (500℃) catalyst was almost equal for octyl ether (2.95%) and oxalic acid 2-ethylhexyl tetradecyl ester (possible product) (2.79%) which were the main products.
- The acidic strength and basic strength both had effect on product distribution and overall conversion. Acidity and basicity were important as the acidic strength and basic strength.
- The highest acidic strength belonged to 75%Al_2O_3-25%SiO_2 (500℃) catalyst which also had the highest basicity. Besides, 25%Al_2O_3-75%SiO_2 (500℃) catalyst had the highest acidity and the highest basic strength.
- The all catalysts were found weak acidic and weak basic solid catalysts.

APPENDIX

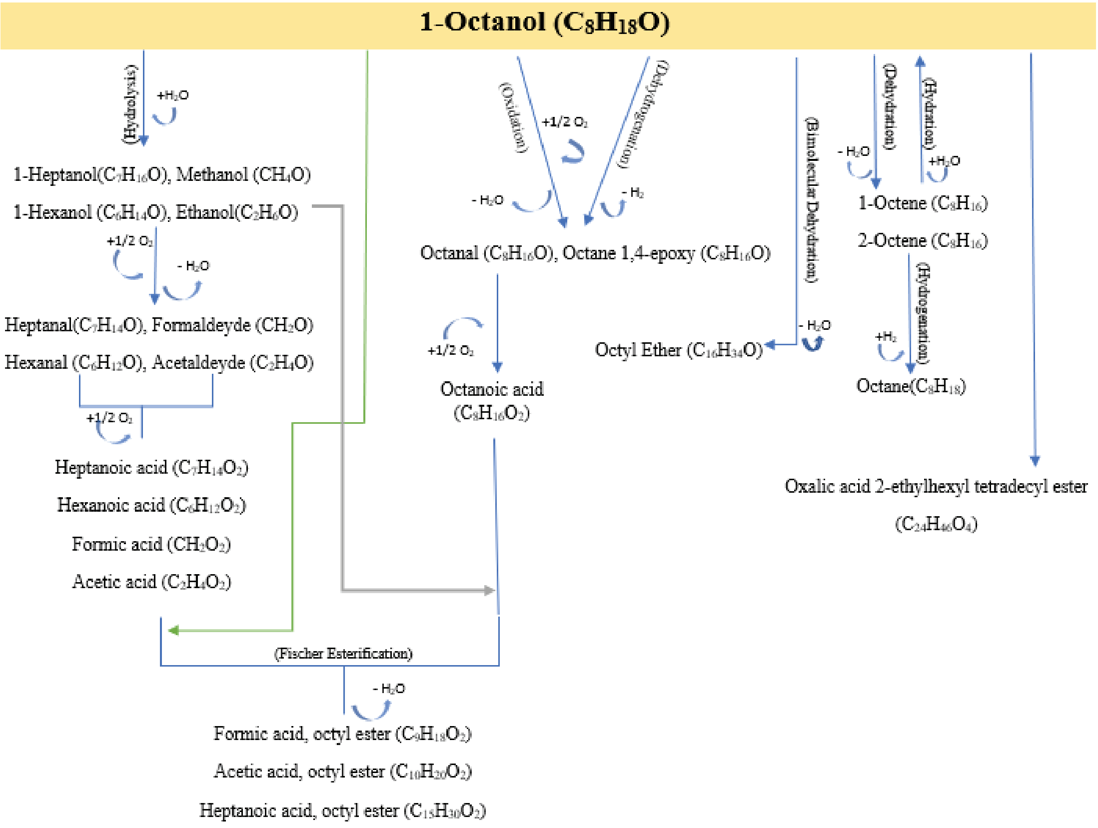

Figure 31. The reaction pathway and possible reactions on 1-octanol over synthesized catalysts.

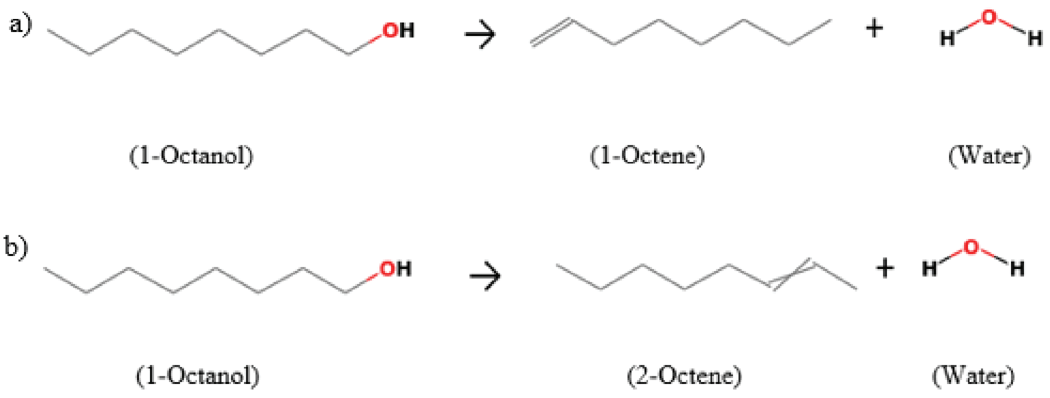

Figure 32. 1-Octanol dehydration reaction to form 1-octene(a) and 2-octene(b) by Saytzeff rule.

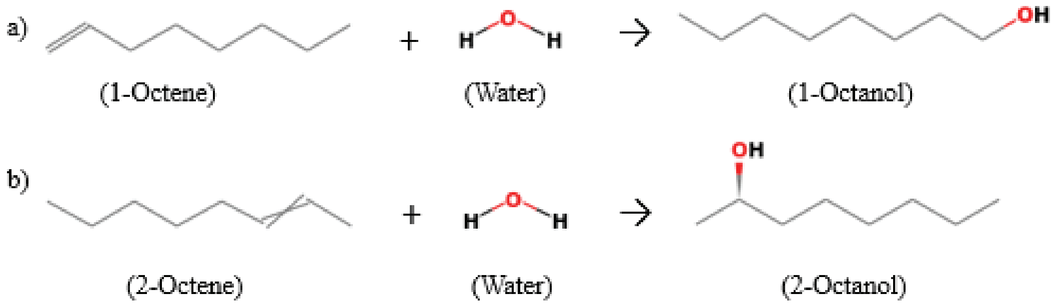

Figure 33. Hydrolysis of 1-octene(a) and 2-octene(b).

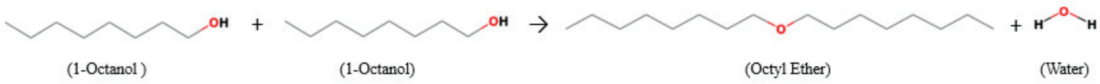

Figure 34. Octyl ether production by bimolecular dehydration reaction.

REFERENCES

1. Osman, A.I., et al., *Silver-Modified η-Al2O3 Catalyst for DME Production.* The Journal of Physical Chemistry C, 2017. **121**(45): p. 25018-25032.

2. Nel, R.J.J. and A. De Klerk, *Dehydration of C5−C12Linear 1-Alcohols over η-Alumina to Fuel Ethers.* Industrial & Engineering Chemistry Research, 2009. **48**(11): p. 5230-5238.

3. Ihmels, E.C. and J. Gmehling, *Compressed Liquid Densities of Methyl tert-Butyl Ether (MTBE), Ethyl tert-Butyl Ether (ETBE), and Diisopropyl Ether (DIPE).* Journal of Chemical & Engineering Data, 2002. **47**(5): p. 1307-1313.

4. Tanabe, K., et al. New Solid Acids and Bases Their Catalytic Properties. Vol. 51. 1989: Elsevier.

5. Wade, L.G., *Organic Chemistry, Fourth Edition (Wade, Jr., L.G.)*. 1987: Upper Saddle River;N.J.: Prentice Hall, c1999. 1377.

6. Vázquez, P., et al., *Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions.* Journal of Molecular Catalysis A: Chemical, 2000. **161**(1): p. 223-232.

7. Gray, W.K., et al., *The Continuous Acid-Catalyzed Dehydration of Alcohols in Supercritical Fluids: A New Approach to the Cleaner Synthesis of Acetals, Ketals, and Ethers with High Selectivity.* Journal of the American Chemical Society, 1999. **121**(46): p. 10711-10718.

8. De Klerk, A., *Contributions of Burtron H. Davis to Fischer–Tropsch Refining Catalysis: Dehydration as Applied to Processes for 1-Octene Production.* Topics in Catalysis, 2014. **57**(6-9): p. 715-722.

9. Pârvulescu, V.I., et al., *Synthesis, characterization and catalytic behavior of SnTf/MCM-41 and SnTf/UVM-7 as new green catalysts for etherification reactions.* Journal of Materials Science, 2009. **44**(24): p. 6693-6700.

10. Veiga, P.M., et al., *Etherification of different glycols with ethanol or 1-octanol catalyzed by acid zeolites.* Molecular Catalysis, 2018. **458**: p. 261-271.

11. Richardson, J.T., *Principles of Catalyst Development* 1ed. Fundamental and Applied Catalysis. 1989: Springer.

12. Lovallo, M.C. and M. Tsapatsis, *Chapter 13 - Nanocrystalline Zeolites: Synthesis, Characterization, and Applications with Emphasis on Zeolite L Nanoclusters*, in *Advanced Catalysts and Nanostructured Materials*, W.R. Moser, Editor. 1996, Academic Press: San Diego. p. 307-343.

13. Hölderich, W.F. and H. van Bekkum, *Chapter 18 Zeolites and related materials in organic syntheses. Brönsted and Lewis Catalysis*, in *Studies in Surface Science and Catalysis*, H. van Bekkum, et al., Editors. 2001, Elsevier. p. 821-910.

14. Kim, Y.-e., et al., *Effect of Ba impregnation on Al2O3 catalyst for 1-octene production by 1-octanol dehydration.* Fuel, 2020. **281**: p. 118791.

15. Sun, J., et al., *Catalysis Chemistry of Dimethyl Ether Synthesis.* ACS Catalysis, 2014. **4**(10): p. 3346-3356.

16. Yurdakoc, M., et al., *Acidity of silica-alumina catalysts by amine titration using Hammett indicators and FT-IR study of pyridine adsorption.* TURKISH JOURNAL OF CHEMISTRY, 1999. **23**(3): p. 319-327.

17. Makgoba, N.P., et al., *Silication of γ-alumina catalyst during the dehydration of linear primary alcohols.* Applied Catalysis A: General, 2006. **297**(2): p. 145-150.

18. Clark J. H., R.C.N., *Clean Synthesis Using Porous Inorganic Solid Catalysts and Supported Reagents*. Clean Technology Centre, Department of Chemistry, University of York, UK Royal Society of Chemistry.

19. Sun, M., et al., *Sol-gel synthesis of macro-mesoporous Al2O3-SiO2-TiO2 monoliths via phase separation route.* Ceramics International, 2016. **42**(14): p. 15926-15932.

20. Alidoust, S., M. Zamani, and M. Jabbari, *Sol-gel synthesis of nanoporous γ-alumina using TX-100 or gelatin/TX-100 mixture as effective catalysts for dehydration of alcohols.* Iranian Journal of Catalysis, 2020. **10**(4): p. 295-305.

21. Landau, M.V., *Sol–Gel Process.* Handbook of Heterogeneous Catalysis, 2008: p. 119-160.

22. Dalton, D.R., *Foundations of Organic Chemistry*, in *Unity and Diversity of Structures, Pathways, and Reactions*.

23. Chen, M., et al., *Dehydration of Long-Chain n-Alcohols to Linear α-Olefins Using Sodium-Modified γ-Al2O3.* Industrial & Engineering Chemistry Research, 2020. **59**(10): p. 4388-4396.

24. Kim, Y.-e., et al., *Production of linear α-olefin 1-octene via dehydration of 1-octanol over Al2O3 catalyst.* Fuel, 2019. **256**: p. 115957.

25. Ruppert, A.M., et al., *Synthesis of long alkyl chain ethers through direct etherification of biomass-based alcohols with 1-octene over heterogeneous acid catalysts.* JOURNAL OF CATALYSIS, 2009. **268**(2): p. 251-259.

26. Bahadori, F. and M. Nalband Oshnuie, *Exergy analysis of indirect dimethyl ether production process.* Sustainable Energy Technologies and Assessments, 2019. **31**: p. 142-145.

27. Casas, C., et al., *Kinetics of the liquid phase dehydration of 1-octanol to di-n-octyl ether on Amberlyst 70.* AIChE Journal, 2017. **63**(9): p. 3966-3978.

28. Bildea, C.S., et al., *Optimal design and plantwide control of novel processes for di-n-pentyl ether production.* Journal of Chemical Technology & Biotechnology, 2015. **90**(6): p. 992-1001.

29. Kwon, E.E., et al., *Sustainable production of alkyl esters via thermal process in the presence of carbon black.* ENVIRONMENTAL RESEARCH, 2020. **183**.

30. Guilera, J., et al., *Synthesis of ethyl octyl ether from diethyl carbonate and 1-octanol over solid catalysts. A screening study.* Applied Catalysis A: General, 2012. **413-414**: p. 21-29.

31. Bringué, R., et al., *Dehydration of 1-octanol to di-n-octyl ether in liquid phase with simultaneous water removal over ion exchange resins: Effect of working-state morphologies.* Applied Catalysis A: General, 2017. **545**: p. 10-16.

32. Perez, M.A., et al., *Ion exchange resins as catalysts for the liquid-phase dehydration of 1-butanol to di-n-butyl ether.* APPLIED CATALYSIS A-GENERAL, 2014. **482**: p. 38-48.

33. Hoek, I., et al., *Kinetics of solid acid catalysed etherification of symmetrical primary alcohols: zeolite BEA catalysed etherification of 1-octanol.* Applied Catalysis A: General, 2004. **266**(1): p. 109-116.

34. Song, W., et al., *Dehydration of 1-Octadecanol over H-BEA: A Combined Experimental and Computational Study.* ACS Catalysis, 2016. **6**(2): p. 878-889.

35. Garbarino, G., et al., *Ethanol and diethyl ether catalytic conversion over commercial alumina and lanthanum-doped alumina: Reaction paths, catalyst structure and coking.* Applied Catalysis B: Environmental, 2018. **236**: p. 490-500.

36. Chokkaram, S., et al., *Conversion of 2-octanol over nickel-alumina, cobalt-alumina, and alumina catalysts.* JOURNAL OF MOLECULAR CATALYSIS A-CHEMICAL, 1997. **121**(2-3): p. 157-169.

37. Kang, M., J.F. DeWilde, and A. Bhan, *Kinetics and Mechanism of Alcohol Dehydration on γ-Al2O3: Effects of Carbon Chain Length and Substitution.* ACS Catalysis, 2015. **5**(2): p. 602-612.

38. Ellis, L.D., et al., *Effects of metal oxide surface doping with phosphonic acid monolayers on alcohol dehydration activity and selectivity.* Applied Catalysis A: General, 2019. **571**: p. 102-106.

39. Shinohara, Y., T. Nakajima, and S. Suzuki, *A theoretical study of the dehydration and the dehydrogenation processes of alcohols on metal oxides using MOPAC.* Journal of Molecular Structure: THEOCHEM, 1999. **460**(1): p. 231-244.

40. Tejero, J., et al., *Dehydration of 1-pentanol to di-n-pentyl ether catalyzed by a microporous ion-exchange resin with simultaneous water removal.* Applied Catalysis A: General, 2006. **308**: p. 223-230.

41. Dorfner, K., *1.2 Synthetic Ion Exchange Resins Ion Exchangers*, K. Dorfner, Editor. 2011, De Gruyter. p. 189-396.

42. Čejka, J., et al., *Advances and challenges in zeolite synthesis and catalysis.* Catalysis Today, 2020. **345**: p. 2-13.

43. Liang, M.N., X.S. Zhu, and W.H. Ma, *The Propylene Oxide Rearrangement Catalyzed by the Lewis Acid Sites of ZSM-5 Catalyst with Controllable Surface Acidity.* CATALYSIS LETTERS, 2019. **149**(4): p. 942-949.

44. Wu, C.-Y. and H.-S. Wu, *Ethylene Formation from Ethanol Dehydration Using ZSM-5 Catalyst.* ACS Omega, 2017. **2**(8): p. 4287-4296.

45. Lee, J., E.J. Jang, and J.H. Kwak, *Acid-base properties of Al2O3: Effects of morphology, crystalline phase, and additives.* Journal of Catalysis, 2017. **345**: p. 135-148.

46. Khaleel, A. and S. Al-Mansouri, *Meso-macroporous γ-alumina by template-free sol–gel synthesis: The effect of the solvent and acid catalyst on the microstructure and textural properties.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2010. **369**(1): p. 272-280.

47. Garbarino, G., et al., *Modification of the properties of γ-alumina as a support for nickel and molybdate catalysts by addition of silica.* Catalysis Today, 2021. **378**: p. 57-64.

48. Poole, C., *Gas Chromatography*. 2012, Saint Louis, UNITED STATES: Elsevier.