Dehydration of Methanol in catalytic fixed bed reactor

Ghassan J hadi
1
1 Northern technical university, Technical institute, Aldour, Iraq

Email: Ghassan.jh@ntu.edu.iq

Abstract. Dimethyl ether (DME) considered as an important alternative fuel and hence, its production is vital. This study directed to choose suitable catalyst (with high selectivity, high energy conservation and low cost) in catalytic dehydration of methanol to produce DME in fixed bed reactor at gas phase. Three commercial catalysts were used (Alumina, Ziolite 5A and resin) and moderate range of temperature (90-120 °C). Weight ratio of catalyst to molar flow rate (W/FA) from 27 to 81 (gcat.hr/gmol) was selected. Both Alumina and ziolite showed weak activity at this range of temperature while resin was better. Conversion of methanol to dimethyl ether (DME) showed significant dependence on increasing temperature and flow rate (highest conversion was 8% at 120 °C and W/F=81 gcat. hr/gmol). Also, deactivation of resin with time was studied at optimum conditions and the results showed no effect of time on both conversion and selectivity to produce DME. DME production selectivity was 100% at all operation circumstances. In addition, the nature of active sites of resin was studied by using selectivity poison procedure. Accordingly, acidic sites were mainly concerned with the reaction whereas Bronsted acidity has mainly contributed to the acidic sites.

1. Introduction
One of the important solutions in future to avoid environmental pollution is using dimethyl ether (DME) as alternative fuels. their properties are very friendly with the environment, no toxic no NOx production [1] also, it progressed on LPG in numerous properties [2]. DME is the least complex ether for arrangement of certain synthetics, for example, dimethyl sulfate. In addition, it has been used as an aerosol propellant to replace chloro fluoro carbons which can destroy the ozone layer [3].

Two methods are used for DME manufacturing, indirect [4] and direct processes [5]. In the indirect process, methanol is converted to DME in a catalytic dehydration reactor over a solid-acid catalyst by the following reaction:

\[ 2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (1) \]

In the direct process, a synthesis gas (a mixture of H2 and CO gases) is used as the feed of the process. In this process, the synthesis gas is mostly converted to methanol and then it is followed by methanol dehydration to DME. The net reaction is as follows:

\[ 3\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2 \quad (2) \]

Dehydration of methanol to produce DME is usually using acid catalysts like Zeolites, silica/aluminas, alumina, metal phosphates and sulfates, and ion exchange resins[6]. Alumina and ziolites show a good methanol conversion and high DME selectivity at high temperature but show less activity at low temperature. Resin shows good activity at low temperature. A good catalyst should
work at low temperature as possible to avoid conversion methanol to olefin or hydrocarbons [7]. Working in low range of temperature (303-423 K) and high selectivity gives resin advantage over the other catalysts [6]. Cation resin used to produce DME from methanol shows good stability with time [7, 8] and no side productions [9]. Wide research has been made particularly in order to find catalysts having higher selectivity for the ether formation and less inclinations to coke formation [1, 10]. For this reason and for other reasons like costs and energy conservation, there is a need to emphasize the resin in this and previous investigations [11, 12].

2. Experimental
In order to achieve this study absolute methanol was utilized as a feedstock and nitrogen was used as a carrier gas, and to purge off the gases from the system.

2.1 Catalysts
Three types of catalysts were used in this investigation. Two of their (alumina and 5A zeolite) are bought from local markets while the resin was supplied from Beiji Refinery; the specifications of the first two catalysts are displayed in Table 1 while the properties of resin are mentioned in [11].

| Type | Structure | Particle density (kg/m³) | Surface area (m²/gm) | Porosity (m³/gm) | Shape | Size (m) |
|------|-----------|-------------------------|----------------------|------------------|-------|---------|
| Catalyst (1) | γ−alumina | Al₂O₃ | 1057 | 201 | 0.745 | Sphere | 5 x 10⁻³ |
| Catalyst (2) | Zeolite (5A) | 0.7CaO·0.3Na₂·0.4Al₂O₃·3SiO₂·4.5H₂O | 914 | 5 | 0.107 | Cylinder | 7 x 2.5 |

Dehydration of methanol was carried out in the gas phase at atmospheric pressure in fixed bed reactor (tubular reactor constructed of QAV glass of an inside diameter 2.54 cm and 100 cm length). First 50 cm filled with glass beads 0.3-0.4 cm diameter regarded as evaporator section. The second section filled pellets of catalyst (40 gm) mixed with some glass beads to support catalyst. Dosing pump of maximum and minimum flow rate 2 and 0.02 liter/hr respectively was used to control flow rate. Condenser was used to condense the vent gases. Both liquid and vapor samples were taken for analyzing. The apparatus of this examination is showing in Figure 1. Tests were investigated by using Gas-fluid chromatography (Shemadzu-9A); a (parapak Q) treated steel section with an outside diameter of (3.17mm) and length of 3m was utilized, The GLC segment was associated with warm conductivity identifier (TCD); the hydrogen was utilized as a carrier gas. Catalytic reaction was carried out at temperature range (90-120 °C) and catalysts with 40 gm (i.e 7cm high), flow rates were 0.02-0.061 L/hr or W/F =27-81 (g cat. hr/ gmol.).

2.2 Experimental Procedure
The dehydration of methanol to produce diethyl ether was carried out in vapor phase , in the beginning nitrogen with flow equal to 150 Liter per hour was used in order to purge off the air from the system and in order to insure a good temperature distribution in the reactor after reaching the desired temperature, then the Nitrogen valve was adjusted to the requested flow rate. A pre specified flow rate of methanol was set on, that vaporization of methanol occurred in the evaporating section of the reactor. The methanol vapor reached over the catalyst bed of the specified temperature, and flow rate. The vapor products passed throughout pipe condensers. The condensed vapor and gases were fed to
gas meter to dissolve traces of reactants and products. All samples were taken double for analysis so that the amount of products could be determined.

![Figure 1. Schematic diagram of the experimental rig.](image-url)
3. Results and discussions

3.1 Comparison between catalysts
Effect of temperature on the three catalysts (Alumina, Ziolite and Resin) conversion was studied at temperature range (90-120 °C) and flow rate W/F=81 gm. Cat .hr/gmol, conversion was calculated according to this equation:

\[
\text{conversion} \% = \frac{\text{Mole of methanol}_{\text{in}} - \text{Mole of methanol}_{\text{out}}}{\text{Mole of methanol}_{\text{in}}} \times 100
\]

As it clears in Figure 2 both Alumina and ziolite did not have a promising activity in the temperature range of 90-120 °C while the resin had significant activity under same circumstances. Maximum conversion of methanol over Alumina was 0.9% at 120 °C but Imperceptible at lower temperatures, Ziolite showed more activity relatively, maximum conversion was 1.7% at 120 °C. Maximum conversion over resin was 8% at same temperature. These results agreed with Hosseiniejad [7] who studied conversion of methanol to DME in autoclave batch reactor. These results consistent with the fact the high conversion of alcohol over Alumina and ziolite need high temperature as it clear in most investigations [10,11,13].

3.2 Effect of reaction time on the activity of the resin catalyst
Activity of the resin at 120 °C and W/F=81 (g cat. hr/ gmol.) was tested with time. High stability was clear within 10 hr continuous reaction as the conversion value remains 8% during these hours and that agrees with Robert [8] who found deactivation of the resin longer than a month insignificant. This stability of conversion with time and significant conversion at low range temperature as shown above encourage to more detailing study for the resin.

3.3 Effect of temperature on the methanol conversion (resin)
Figure 3 shows the correlation between conversion and temperature in the range (90-120 °C) at different values of feed flow rate over resin. This figure shows that conversion increments with expanding temperature at steady W/F to maximum value 8% at 120 °C and (W/F = 81). Figure 4 shows methanol conversion according to flow rate. The figure indicates that conversion increases with

![Figure 2. Effect of temp. on methanol conversion (W/F=81).](image-url)
increasing W/F at any temperature and maximum amount happens in the temperature 120 °C. This increasing is due to the increase in the contact time.

![Figure 3](image1.png)

**Figure 3.** Effect of Temp. on methanol conversion over Resin.

![Figure 4](image2.png)

**Figure 4.** Effect of W/F on methanol conversion over Resin.

3.4 **Selectivity and reaction rate**

Selectivity of DME was always 100% at all reaction conditions (i.e. no side products were noticed). These results agreed with many researchers [8] and [9] and it often due to the low temperature used. Side products were founded in small amounts by many workers [14] and [15] when alumina and ziolite used at high temperatures.
The rate of methanol consumption was determined dependent on material balance. Figure 5 show the relationship between methanol reaction rate (\(r_A\)) versus temperature over resin catalyst. The figure shows \(r_A\) growths with increasing temperature in all variable flow, this also attributed to the increase in the contact time as mentioned previously.

3.5 Nature of active site

To recognize the nature of active sites, poisoning them selectively were used. As well-known pyridine adsorb reversibly on OH group and irreversibly on acidic sites [16]; by this way pyridine allow distinction between them. Water used for the same purpose due to strong affinity of water to SO\(_3\)H the number of sites available for chemisorption of methanol are reduced [17]. Figure 6 shows decreasing of methanol conversion with increasing percent of pyridine and/or water, this implies methanol conversion mainly related with the acid sites.

To check the Lewis and Bronsted acidic sites, role cations like (Li, K and Na) were used to exchange protons in resin. A 1N solution of the chloride salts were passed through the resin at 90C, 500% excess of exchanging caution equivalents was used. The rate was 1.3 liter per 100g of resin per hour. Exchanged resin was washed with deionized water till negative test for chloride ion was obtained in the washed water with 10% silver nitrate[18]. By this way it is ensured that all protons have been replaced. Experiments showed the conversion of methanol dropped to 0% with any cation was replaced, which mean conversion reaction mainly concerned with the proton.
4. Conclusions
Both Alumina and ziolite showed low activity at used temperature range (90-120 °C) with 0.9% and 1.7% maximum conversion for Alumina and ziolite respectively, but Resin was more active than them (with maximum conversion 8%). Methanol conversion and DME selectivity didn’t affected by long time operation and DME selectivity was 100% at all operation conditions which attributed to low temperatures used. In addition, the study showed methanol conversion over resin highly depend on temperature and flow rate so that was 1.5% at 90 °C and W/F=32 but was 8% at 120 °C and W/F=81. The study of nature of active site showed that methanol conversion over resin was mainly concerted with acid sites (Bronsted acid).

References
[1] Fleisch T H, Basu A, Gradassi M J and Masin J G 1997 Dimethyl ether: A fuel for the 21st century Stud. Surf. Sci. Catal. 107 117–25
[2] Ardy A, Pohan R D A, Rizkiana J, Laniwati M and Susanto H 2019 Dehydration of methanol to dimethyl ether (DME): Performance of three types of catalyst at atmospheric pressure AIP Conf. Proc. 2085 2–7
[3] Semelsberger T A, Borup R L and Greene H L 2006 Dimethyl ether (DME) as an alternative fuel J. Power Sources 156 497–511
[4] Berčič G and Levec J 1993 Catalytic Dehydration of Methanol to Dimethyl Ether. Kinetic Investigation and Reactor Simulation Ind. Eng. Chem. Res. 32 2478–84
[5] Takeguchi T, Yanagisawa K I, Inui T and Inoue M 2000 Effect of the property of solid acid upon syngas-to-dimethyl ether conversion on the hybrid catalysts composed of Cu-Zn-Ga and solid acids Appl. Catal. A Gen. 192 201–9
[6] Spivey J J 1991 Review: Dehydration catalysts for the methanol/dimethyl ether reaction Chem. Eng. Commun. 110 123–42
[7] Hosseininejad S, Afacan A and Hayes R E 2012 Catalytic and kinetic study of methanol dehydration to dimethyl ether Chem. Eng. Res. Des. 90 825–33
[8] Kabel R L and Johanson L N 1962 Reaction kinetics and adsorption equilibria in the vapor-phase dehydration of ethanol AIChE J. 8 621–8
[9] Gates B C and Johanson L N 1971 Langmuir-hinshelwood kinetics of the dehydration of methanol catalyzed by cation exchange resin AIChE J. 17 981–3
[10] Palomo J, Rodríguez-Mirasol J and Cordero T 2019 Methanol dehydration to dimethyl ether on Zr-loaded P-containing mesoporous activated carbon catalysts Materials (Basel). 12
[11] Hadi G J 2007 Kinetic Study of Catalytic Dehydration of Ethanol in Fixed Bed Catalytic Reactor
[12] Zablouka M A, Kaseera N W, Hadi G J and Hadi A J 2011 Comparison the Performance of Four Catalyst Types in the Catalytic Dehydration of Ethanol 1 137–49
[13] Sierra I, Ereña J, Aguayo A T, Ateka A and Bilbao J 2013 Kinetic modelling for the dehydration of methanol to dimethyl ether over γ-Al2O3 Chem. Eng. Trans. 32 613–8
[14] Jiang S, Hwang J S, Jin T, Cai T, Cho W, Baek Y S and Park S E 2004 Dehydration of Methanol to Dimethyl Ether over ZSM-5 Zeolite Bull. Korean Chem. Soc. 25 185–9
[15] Dai W, Kong W, Wu G, Li N, Li L and Guan N 2011 Catalytic dehydration of methanol to dimethyl ether over aluminophosphate and silico-aluminophosphate molecular sieves Catal. Commun. 12 535–8
[16] Anon Pichat, P., Ph.D thesis, university of Lyon. 1966.
[17] Vaidya S H, Bhandari V M and Chaudhari R V. 2003 Reaction kinetics studies on catalytic dehydration of 1,4-butanol using cation exchange resin Appl. Catal. A Gen. 242 321–8
[18] Rudham R and Spiers A I 1997 Catalytic dehydration of propan-2-ol by lanthanum-Y zeolite J. Chem. Soc. - Faraday Trans. 93 1445–8