

Effects of catalyst particle size on methanol dehydration at different temperatures and weight hourly space velocities

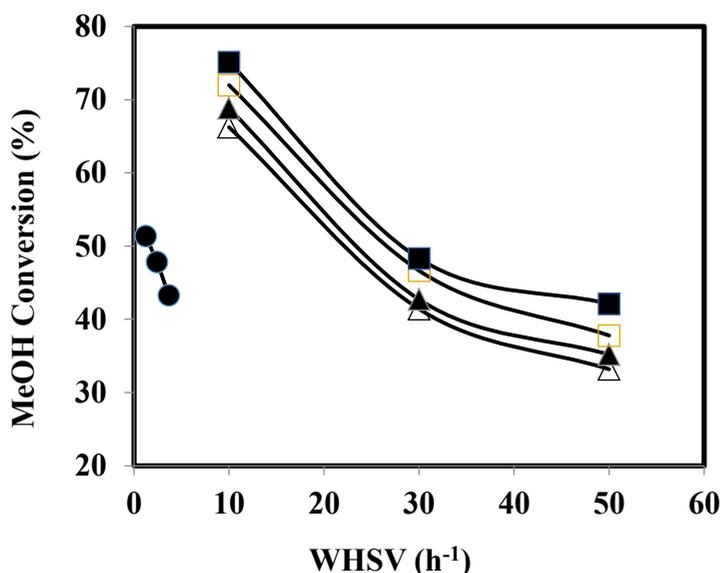
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HIGHLIGHTS

- Effect of catalyst particle size on methanol conversion was investigated.
- Conversion of methanol in micro-channel reactor was measured.
- Methanol conversion in fixed bed and micro-channel reactor was compared.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of catalyst particle size on dehydration of methanol to dimethyl ether is investigated using fixed bed and micro-channel reactors at different temperatures and weight hourly space velocities. The experiments were carried out at 290 and 320°C. The space velocities were changed from 10 up to 90h⁻¹ and from 1.22 to 3.65h⁻¹ for fixed bed and micro-channel reactors, respectively. Considering the catalyst particle size effect on dehydration reaction, the particle size was changed from 0.063 to 1mm. Commercial gamma alumina was used as catalyst in all the experiments. The fabricated micro-channel reactor had 40 channels with 1mm diameter and 6 cm length. The channels were sub-coated with alumina and finally were coated with gamma alumina as dehydration catalyst. The results showed that methanol conversions were increased by increasing the temperature and decreasing the particle size of the catalyst. Furthermore, methanol conversion in micro-channel reactor was less than for fixed bed reactor under the similar WHSVs, due to the special geometrical shape of the micro-channels.

1. Introduction

Dimethyl ether (DME) or CH_3OCH_3 , also known as methoxymethane, wood ether, dimethyl oxide or methyl ether, is a non-toxic liquefied gas. At 1 atm and 25°C dimethyl ether is a gas [1]. Moreover, methanol can be replaced by DME as primary substance for production of hydrocarbons such as light olefins, and chemicals such as dimethyl sulphate, methyl acetate [2]. Also, DME can be used as a source of hydrogen for fuel cells [2]. Due to its high cetane number (>55) this compound is considered as an alternative fuel for diesel engines [3].

Generally, two direct and indirect methods are used for dimethyl ether production [4-8]. In direct method, some serial reactions occur such as methanol formation, methanol dehydration and water gas shift (WGS). Methanol is produced in the middle path of the mentioned serial reactions and finally is dehydrated to DME [8, 9]. These reactions can be simplified as follows:

(1)

Indirect method is a simple reaction for DME production, where methanol is dehydrated by using an acidic catalyst such as H-ZSM-5 and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$). Between two mentioned solid acid catalysts, activity of H-ZSM-5 is more than the other one. However, fast deactivation of strong acidic sites of H-ZSM-5 is one of its weaknesses as compared to gamma alumina [10].

Methanol dehydration is a slight exothermic reaction, so that:

(2)

From transport phenomena point of view, catalyst particle size has an important role on global kinetic rate of a heterogeneous reaction. Whereas, there are little information about the effect of catalyst particle size on methanol dehydration. In this work, fixed bed reactor tests were carried out to investigate the effect of gamma alumina grain size (G. S.) on methanol dehydration at two different temperatures and weight hourly space velocities (WHSV). In all of experiments the methanol flow rate was kept constant but temperature and WHSVs were changed. In the second part of this work, a micro-channel reactor was fabricated and its channels were coated by gamma alumina. By using this reactor, the effects of temperature and WHSV were investigated on

methanol conversion and the results were compared with the results obtained from the fixed bed reactor.

2. Experimental

2.1. Fixed Bed Reactor

All of the experiments were carried out in an isothermal fixed bed reactor ($\frac{3}{4}$ inch diameter) which was previously used by Eliassi *et al.* [11]. In this system pure methanol was pumped from the methanol feed tank at a rate of 63cc/h to an evaporator. The evaporated methanol was sent to a super-heater before flowing to the isothermal fixed bed reactor. A thermo well and a thermocouple system was used in order to control the reactor temperature. Reactor products were passed through a cooler to cool down to the room temperature. Then the liquid and gas products were separated into the trap. Experiments were carried out at 290 and 320°C under the constant atmospheric pressure.

2.2. Micro-Channel Reactor

A micro-channel reactor is an apparatus which has a sandwich construction and contains several channels. Usually, diameter of these channels are less than 1mm and after that a catalyst layer was coated on these channels, the reactor can be used for considering the various chemical reactions [12-13]. In this work, a micro-channel reactor was made by using titanium plate, which 40 parallel micro-channels in this plate were made by milling and lathing process. The diameter and length of each channel were 1 mm and 40 mm, respectively. Fig. 1. shows perspective picture of the made micro-channel plates.

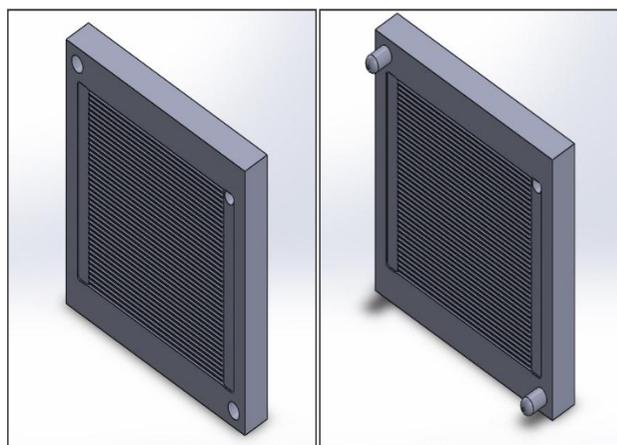


Fig. 1. Perspective of the fabricated micro-channel plates

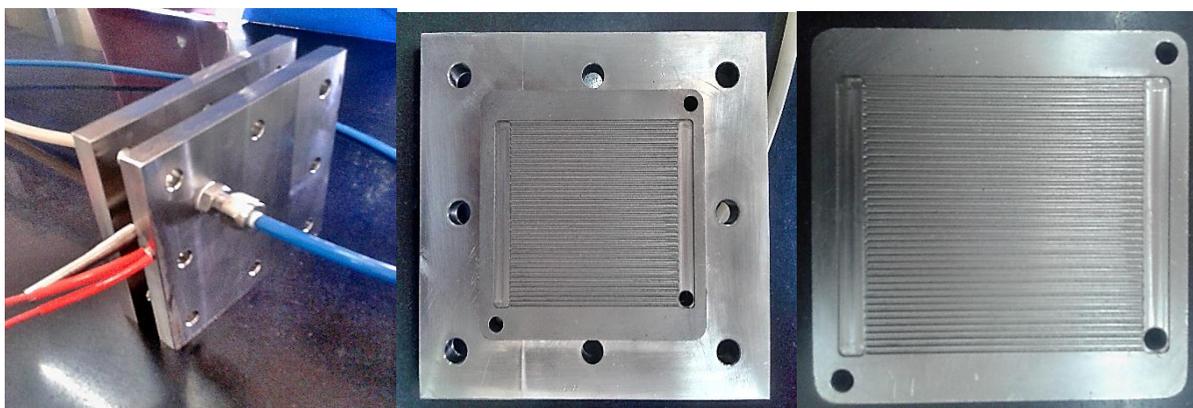


Fig. 2. Micro-channel reactor with jaw plates, connections, heater and thermocouples

The feed was injected to the reactor through a hole near the vertex of the titanium plate and the products exit from another hole which is placed on the opposite side of the entrance hole. Fig. 2 shows the fabricated micro-channel reactor with jaw plates, connections, heater and thermocouples. The micro-channel reactor set up is made of the following components: syringe pump (Irman tech, Iran) for methanol injection, heater, thermocouples, temperature controller and gas-liquid separation vessel.

Micro-channel coating is an important step for fabrication of these types of reactor. It is required that the coated catalyst forms a uniform and stable layer on the reactor channels. In this work, a thin layer of gamma alumina was coated on the channels by using catalyst slurry mixture. Usually, for increasing specific surface area and mechanical resistance, a nano-porous oxide used as sub-layer on the channels [14]. For this purpose, an alumina sol was prepared via sol-gel method by aluminum iso-propoxide (AIP) and iso-propanol as a solvent. To prepare the sol, initially AIP and isopropanol was mixed for 30 minutes at 65-70°C by a sonicator. Acetic acid, propanoic acid and double distilled water were used to control the pH. Also, ethyl acetate was used as a surfactant for increasing sol adhesion to the micro-channels. Then the sol was applied on the micro-channels by injection method and finally the plates were dried in an oven. In the second step, the powder of gamma alumina was used to preparation of slurry of the catalyst. The particle size of the gamma alumina powder was less than 40 microns. Similar to the previous mentioned coating procedure, the prepared slurry was injected to the channels and the plates were placed in the furnace for 3 hours for calcination at 350°C.

2.3 Materials

Commercial extruded gamma alumina was prepared from BASF, Germany (Kat D10-10 S4), aluminum iso-propoxide (AIP) and iso-propanol from Merck and methanol from Iran Petrochemical Company.

2.4 Experimental Conditions

In the fixed bed reactor, the experiments were performed by using four different catalyst particle sizes (P.S.) less than 0.063 up to 1mm, namely: $0.5 < P.S. < 1\text{mm}$, $0.125 < P.S. < 0.5\text{mm}$, $0.063 < P.S. < 0.125\text{mm}$ and $P.S. < 0.063$. Also, the reactor temperature was fixed on 290 and 320°C. All of experiments were carried out by 63cc/h methanol as the feed of the reactor, but WHSV (ratio of methanol mass flow rate to the mass of the used catalyst) were changed from 10 up to 90 h⁻¹.

The experiments were repeated three times and the average of the obtained results were reported as the measured quantity.

The experiments in micro-channel reactor were carried out at 290 and 320°C and methanol flow rates in micro-reactor were fixed on 1, 2 and 3ml/h. Also, WHSV values were 1.22, 2.43 and 3.65 h⁻¹.

3. Results and discussion

Figures 3- 6 show the changes of methanol conversion versus WHSV at different temperature and catalyst particle size in fixed bed reactor.

It is worth noting that all of experiments in fixed bed reactor were carried out at constant methanol flow rates and WHSVs were changed just by changing amount of the loaded catalyst. Methanol conversion (X) and WHSV are defined as:

$$\text{---} \quad (3)$$

$$\text{---} \quad (4)$$

where, F_{in} , F_{out} and m_c are the methanol mass flow rates at inlet and outlet of the reactor and the mass of the loaded catalyst, respectively.

Figures 3- 6 clearly show that by increasing temperature, the methanol conversion increased rapidly.

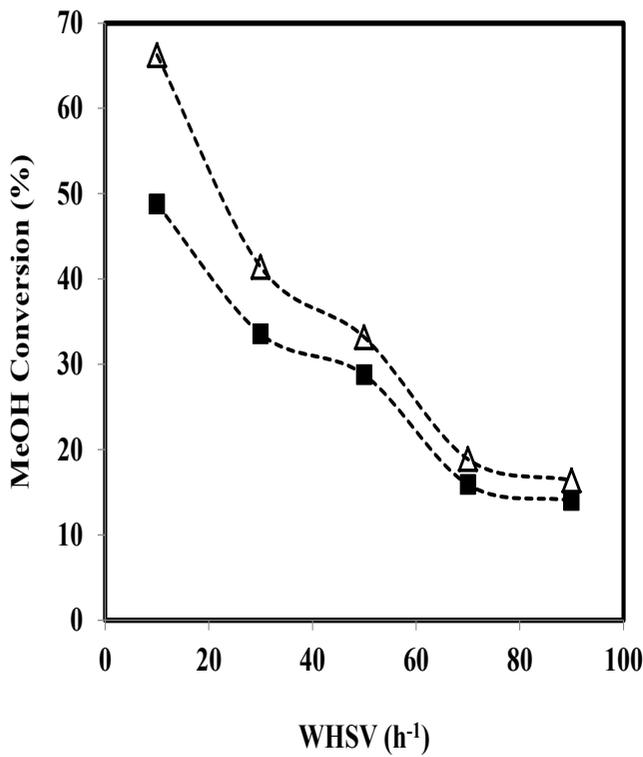


Fig. 3. Methanol conversion versus WHSV at 290°C (■) and 320°C (Δ) in the fixed bed reactor for catalyst particle size of 0.5<P.S. <1mm. Dotted lines show the trend of changes

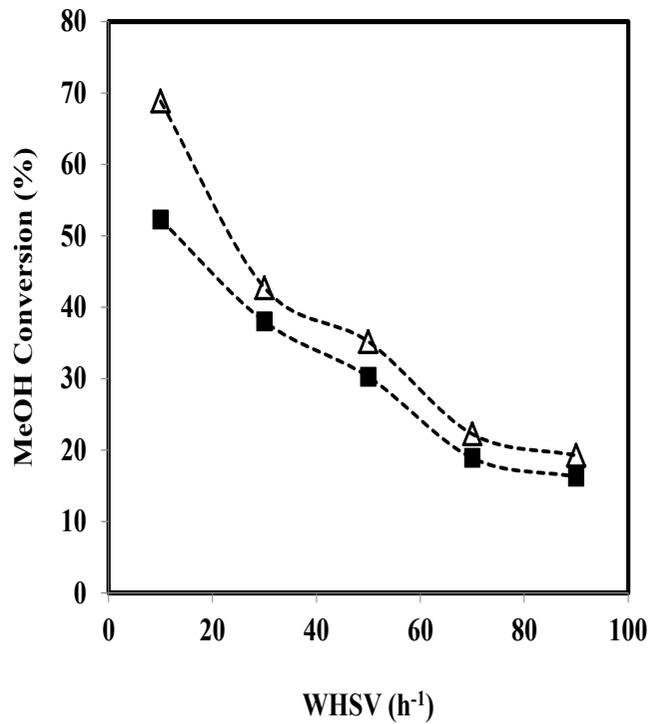


Fig. 4. Methanol conversion versus WHSV at 290°C (■) and 320°C (Δ) in the fixed bed reactor for particle size of 0.125<P.S. <0.5mm. Dotted lines show the trend of changes..

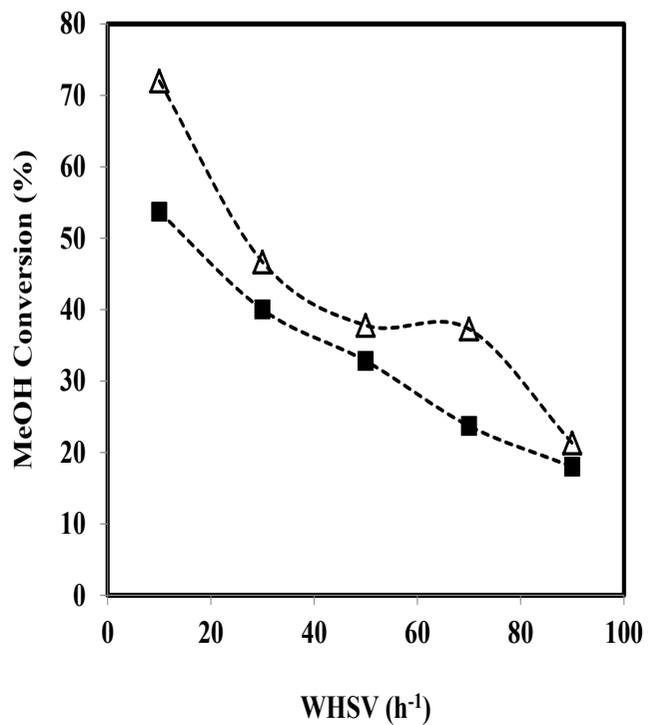


Fig. 5. Methanol conversion versus WHSV at 290°C (■) and 320°C (Δ) in the fixed bed reactor for catalyst particle size of 0.063<P.S. <0.125mm. Dotted lines show the trend of changes.

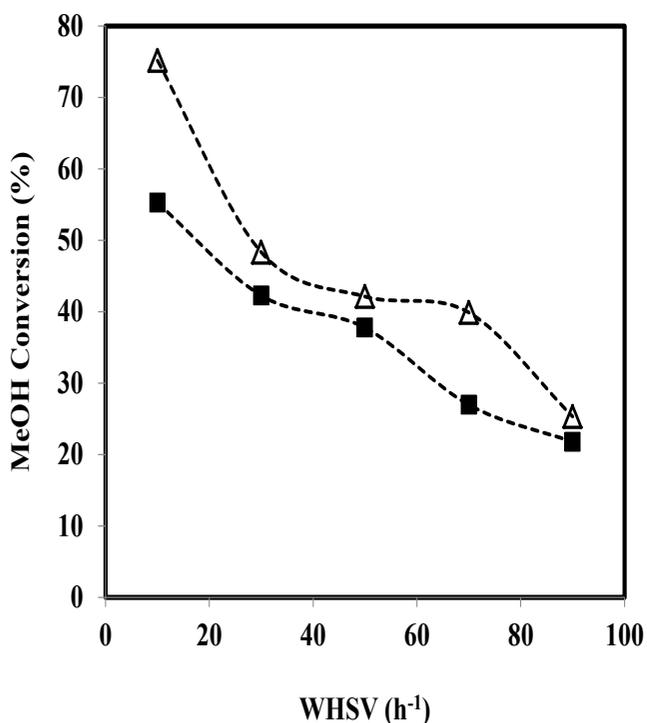


Fig. 6. Methanol conversion versus WHSV at 290°C (■) and 320°C (Δ) in the fixed bed reactor for catalyst particle size of P.S. <0.063mm. Dotted lines show the trend of changes

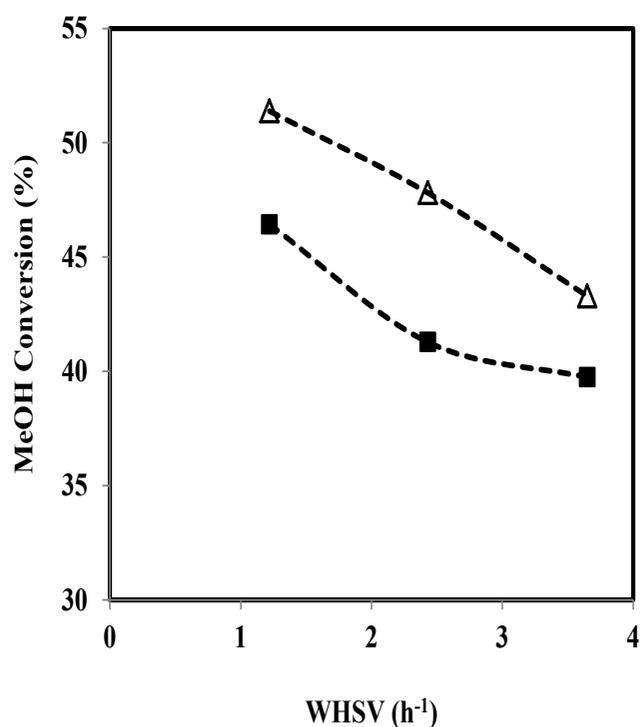


Fig. 7. Methanol conversion changes versus WHSV in micro-channel reactor at 290°C (■) and 320°C (Δ). Dotted lines show the trend of changes

Also, these figures show that the methanol conversion increased by decreasing of the catalyst particle size. For example, according to Figure 6, at 290°C and $\text{WHSV}=10\text{h}^{-1}$, the conversion is reached to 55.25% , when the catalyst particle size is less than 0.063mm. While, according to Fig. 3, for $0.5 < \text{P.S.} < 1\text{mm}$ and at the same conditions (temperature and WHSV) the methanol conversion is reached to 48.77%. In the other word, in the second case, the methanol conversion was decreased about 12%. With notice to this matter that the methanol flow rates were the same in the both experiments, the observed changes can be related to two different phenomena. One of them is that the available surface of the catalyst particles for the reactant molecules were increased for the smaller catalyst particles. The second phenomenon can be related to increasing mass transfer coefficient by decreasing the catalyst particle size, because, the flow pattern of the gases (reactants and/or products) can be affected by catalyst particle sizes in the fixed bed reactor. In the second series of experiments, the micro-channel reactor was used. In these experiments, the mass of the coated catalyst was nearly constant and WHSVs were changed by changing the methanol flow rates. The obtained results are given in Figure 7. By using this reactor, the average increasing of methanol conversion was about 5% by changing temperature from 290 to 320°C.

Figure 8 shows methanol conversion versus WHSV for fixed bed reactor in compared with micro-channel reactor at 290°C. According to this figure, at the same WHSVs, methanol conversion is higher for fixed bed reactor than micro-channel reactor. This fact can be related to the geometrical shape of the channels, so that the pressure drop through different channels was not to be the same and all of the channels were not available for the reactant molecules and finally the conversion was decreased. This claim can be approved by considering the status of the channels after the reaction. Figure 9 shows a picture of the micro-channel reactor after using the dehydration reaction. With notice to the color changes of the catalyst at different channels, it can be seen that more than half of the channels were not available for the reaction. In the other word, the real WHSV for this reactor is more than that was reported initially and this fact was caused to methanol conversion decreasing. It seems that by changing the geometrical shape of the channels and decreasing the pressure drop, the methanol conversion will be increased. Non-uniform coating of the catalyst on the surface of the channels is the other fact for different pressure drop in different channels. Therefore, by improving the coating techniques the conversion can be increased. Also, mass transfer coefficient is another important factor in reaction rate of a heterogeneous reaction and it can

be influenced by flow rate of the reactants in the reactor. Since the flow rate of methanol in fixed bed and micro-channel reactors were different, therefore, mass transfer coefficients in two reactors are not the same, as a results, methanol conversions in two reactors were different, whereas the WHSVs were the same.

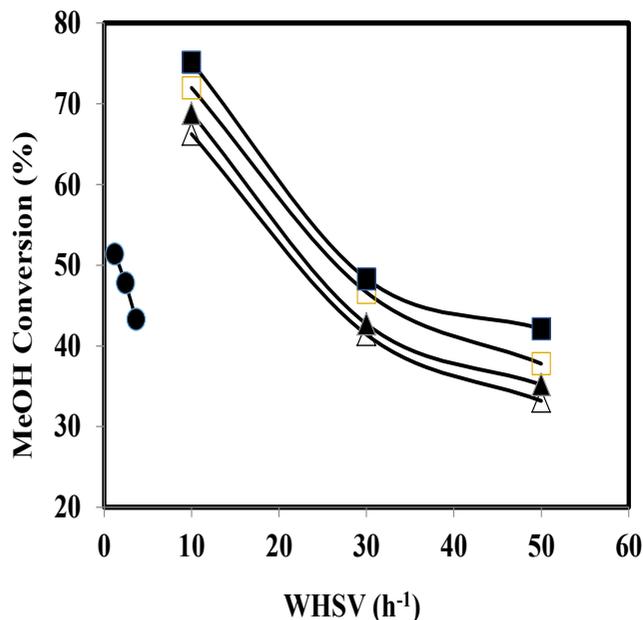


Fig. 8. Methanol conversion versus WHSV for fixed bed reactor in comparison with micro-channel reactor at 290°C. Micro-channel reactor (●). Fixed bed reactor: P.S. < 0.063 mm (■), 0.063 < P.S. < 0.125 mm (□), 0.125 < P.S. < 0.5 mm (▲), 0.5 < P.S. < 1 mm (Δ).



Fig. 9. White channels were not used during methanol dehydration

4. Conclusions

Effects of commercial gamma alumina particle size as a catalyst for dehydration of methanol to DME were investigated. For this purpose the reaction was performed in a fixed bed reactor at two different temperatures and different weight hourly space velocities. The results showed that methanol conversion was increased by decreasing catalyst particle size. This phenomenon can be interpreted by increasing the effective surface area of the catalyst by its size reduction. Also, methanol conversion in fixed bed reactor was more than for micro-channel reactor. This phenomenon can be due to the: (a) non-uniform coating of the catalyst on the surface of the channels and non-uniform pressure drop in different channels (b) some of the channels were not available for reactants during the dehydration reaction for geometry of the micro-channel reactor (c) flow rate of the reactants in the channels was different in compare with the fixed bed reactor.

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References

- [1] L. C. L. Agostinho, C. Barbosa, L. Nascimento, J. Rodbari, Catalytic Dehydration of Methanol to Dimethyl Ether (DME) Using the Al₆₂,2Cu₂₅,3Fe₁₂,5 Quasicrystalline Alloy, *Journal of Chemical Engineering & Process Technology* 4, 164 (2013) 7-8.
- [2] J. Ereña, I. Sierra, M. Olazar, A. G. Gayubo, A. T. Aguayo, Deactivation of a CuO-ZnO-Al₂O₃/γ-Al₂O₃ catalyst in the synthesis of dimethyl ether, *Industrial & Engineering Chemistry Research* 47 (2008) 2238-2247.
- [3] F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard, Synthesis of dimethyl ether from methanol over aluminium phosphate and silica-titania catalysts, *Catalysis Communications* 6 (2005) 542-549.
- [4] F. Dadgar, R. Myrstad, P. Pfeifer, A. Holmen, J. V. Hilde, Direct dimethyl ether synthesis from synthesis gas: The influence of methanol dehydration on methanol synthesis reaction, *Catalysis Today* 270 (2016) 76-84.
- [5] D. Macina, Z. Piwowarska, K. Tarach, K. Góra-Marek, J. Ryczkowski, L. Chmielarz, Mesoporous silica materials modified with alumina polycations as catalysts for the synthesis of dimethyl ether from

- methanol, *Materials Research Bulletin*, 74 (2016) 425-435.
- [6] Z. Hosseini, M. Taghizadeh, F. Yaripour, Synthesis of nanocrystalline γ - Al_2O_3 by sol-gel and precipitation methods for methanol dehydration to dimethyl ether, *Journal of Natural Gas Chemistry* 20 (2011) 128-134.
- [7] Q. Tang, H. Xu, Y. Zheng, J. Wang, H. Li, J. Zhang, Catalytic dehydration of methanol to dimethyl ether over micro-mesoporous ZSM-5/MCM-41 composite molecular sieves, *Applied Catalysis A: General* 413 (2012) 36-42.
- [8] Y. Tavan, R. Hasanvandian, Two practical equations for methanol dehydration reaction over HZSM-5 catalyst—Part I: Second order rate equation, *Fuel* 142 (2015) 20-214.
- [9] F. Yaripour, Z. Shariatinia, S. Sahebdehfar, A. Irandokht, The effects of synthesis operation conditions on the properties of modified γ -alumina nanocatalysts in methanol dehydration to dimethyl ether using factorial experimental design, *Fuel* 139 (2015) 40-50.
- [10] B. Sabour, M. H. Peyrovi, T. Hamoule, M. Rashidzadeh, Catalytic dehydration of methanol to dimethyl ether (DME) over Al-HMS catalysts, *Journal of Industrial and Engineering Chemistry* 20 (2014) 222-227.
- [11] F. Raoof, M. Taghizadeh, A. Eliassi, F. Yaripour, Effects of Temperature and Feed Composition on Catalytic Dehydration of Methanol to Dimethyl Ether over Gamma-Alumina, *Fuel* 87 (2008) 2967-2971.
- [12] P. L. Mills, D. J. Quiram, J. F. Ryley, Microreactor technology and process miniaturization for catalytic reactions—a perspective on recent developments and emerging technologies, *Chemical Engineering Science* 62 (2007) 6992-7010.
- [13] A. I. Stankiewicz, J. A. Moulijn, Process intensification: transforming chemical engineering, *Chemical Engineering Progress* 96 (2000) 22-34.
- [14] K. Haas-Santo, M. Fichtner, K. Schubert, Preparation of microstructure compatible porous supports by sol-gel synthesis for catalyst coatings, *Applied Catalysis A: General* 220 (2001) 79-92.