

DME Synthesis over MSU-S Catalyst through Methanol Dehydration Reaction

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Abstract

MSU-S mesoporous catalyst with $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio of 55 was synthesized using tetrapropylammonium hydroxide (TPAOH) as a structure directing agent and hexadecyltrimethylammonium bromide (CTAB) as a surfactant. The catalytic activity of the calcined sample was evaluated for the dehydration of methanol to dimethyl ether (DME) in a vertical fixed bed microreactor at a weight hourly space velocity (WHSV) of 5 hr^{-1} . Temperature ranged from $230 \text{ }^\circ\text{C}$ to $380 \text{ }^\circ\text{C}$ and pressure was kept constant at 1 bar. The catalyst was characterized by XRD; consequently, the mesoporous structure of MSU-S catalyst was verified. The activity, selectivity, and stability of MSU-S catalyst were investigated in a vertical fixed bed reactor. An increase in methanol conversion was observed by increasing temperature. The equilibrium conversion of methanol was almost reached at $380 \text{ }^\circ\text{C}$ and selectivity decreased from 100% to 97% as temperature rose from $200 \text{ }^\circ\text{C}$ to $380 \text{ }^\circ\text{C}$. The stability of MSU-S (Michigan State University) catalyst was investigated for 12 hr at $380 \text{ }^\circ\text{C}$ and a stable methanol conversion was observed during the mentioned time.

Keywords: MSU-S, DME Synthesis, Mesoporous Material

1. Introduction

Dimethyl ether (DME) has been found as a potential alternative to diesel engine fuels because of its benign properties to the environment (Ha et al., 2011). Moreover, DME is used in some petrochemical processes like isomerization, alkylation, hydroforming, and catalytic cracking (Chuah et al., 2000). It can be considered as a substitute for chlorofluorocarbons and LPG (Hassanpour et al., 2010). DME is a colorless, volatile, and non-peroxide-forming chemical which burns with a visible blue flame. It is also non-toxic, non-carcinogenic, and non-teratogenic (Raof et al., 2008).

Two ways are used to convert methanol to DME, namely direct and indirect processes (Naik et al., 2010; Raof et al., 2008). In the indirect process, one mole of methanol is dehydrated to water and DME in a fixed bed microreactor over a solid acid catalyst like γ -alumina, modified alumina with silica and phosphorous, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, and zeolites like chabazites, mordenites, SAPO's, H-ZSM-5, and H-Y (Hassanpour et al., 2010; Mao et al., 2009).

The second method employs a hybrid catalyst which converts synthesis gas to methanol as an intermediate, and methanol is then dehydrated to DME (Ramos et al., 2005). The catalyst of the direct process is typically $\text{Cu/ZnO/Al}_2\text{O}_3$ (Fu et al., 2005).

Researchers are trying to discover novel catalysts for the production of DME from methanol having a higher activity, selectivity, and stability towards water (Moradi et al., 2010). On the other hand, recent

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discoveries have shown that mesoporous catalysts are potential candidates either as active sites or catalyst support for various processes. The pore dimensions of these mesoporous materials are flexible and can be adjusted between 15 to 100 Å due to their usage; however, the inherent acidity of these materials is not as strong as zeolites (Wang et al., 2010). MSU-S (Michigan state university) (Liu et al., 2001) and mesoporous alumina silicate (MAS) (Zhang et al., 2010) are two of the enhanced mesoporous materials which show higher acidity than the previously synthesized mesoporous catalysts. Nanoclustered zeolite precursors have been applied directly to the synthesis of MSU-S and MAS (Wang et al., 2010). The worm-like characteristic of MSU-S is also different and it has long range ordered hexagonal arrays of MCM-41 (Taguchi and Schüth, 2005).

The MSU-S mesoporous aluminosilicates synthesized by the incorporation of zeolite seeds exhibit high hydrothermal stability and increased acidity compared to conventional Al-MCM-41. With regard to acidity, the MSU-S materials were more active in some catalytic processes compared to Al-MCM-41 with a similar Al content, which indicates the higher acidity strength of the MSU-S materials. Therefore, MSU-S material can be considered as a good choice for catalytic processes (Triantafyllidis et al., 2007).

MSU-S catalyst activity in methanol to DME reaction has not been studied yet. In this work, MSU-S catalyst was synthesized and characterized by XRD, and was then tested in a microreactor for the dehydration of methanol to DME.

2. Experimental

2.1. Catalyst preparation

Mesoporous MSU-S (MFI) catalyst was synthesized analogous to the synthesis procedure described by (Liu et al., 2001). 10.2 gr. of tetrapropylammonium hydroxide (TPAOH, Merck, 40% aqueous solution) as an MFI structure director was added to 79.26 gr. of deionized water. Then, 0.34 gr. of sodium aluminate and 6.0 gr. of Cab-osil M5 as aluminum and silicon sources were respectively added to the solution of water and TPAOH. The final mixture was kept under stirring at 50 °C for 18 hours so that zeolite MFI seeds were formed. Then, 100 gr. of deionized water and 9.44 gr. of hexadecyltrimethylammonium bromide (HTABr) as surfactant were mixed and introduced to the seeds suspension to assemble mesopores.

The final gel with the molar composition of 1 SiO₂: 0.018 Al₂O₃: 0.023 Na₂O: 0.266 HTABr: 0.2 TPAOH: 103.6 H₂O was introduced to a Teflon-lined stainless steel autoclave and placed into an oven at 150 °C for 48 hrs.

The product was washed with distilled water, filtered, and dried at 80 °C for 8 hrs; the white powder was then ion exchanged with a solution of 0.1 M NH₄NO₃ in 96% ethanol at reflux temperature for 2 hrs. The product was dried at 90 °C for 12 hrs and the dried samples were calcined at 550 °C in air for 10 hrs in a muffle furnace at a heating rate of 1 °C/min.

2.2. Characterization

The X-ray diffraction (XRD) analysis of the calcined catalyst was performed in the 2θ range of 0-10° by using an X-PERT diffractometer employing Ni-filtered Cu Kα radiation at 40 kV and 40 mA.

2.3. Experimental setup

A scheme of the experimental setup has been shown in Figure 1, which consists of an HPLC pump with the accuracy of 0.01 (ml/min); this accuracy enables us to easily regulate the flow rate of methanol at the desired amount. Methanol is pumped to a preheater to vaporize and is then sent to the

reactor. An online gas chromatography (GC) is connected to the outlet of the reactor to detect the products. The lines between preheater and reactor and outlet lines from the reactor to GC are heat traced in order to lower the heat loss and avoid condensation of products.

2.4. Activity test

Vapor phase methanol dehydration reaction was performed in a vertical fixed bed microreactor (tubular, 200 mm length, and 9 mm internal diameter) in temperature range of 200 °C to 380 °C and atmospheric pressure. 1.5 gr. of MSU-S catalyst was loaded to the reactor with quartz wool placed at the top and the bottom of the reactor. The reactor was equipped with a thermocouple placed inside the reactor through the bed of the catalyst. Prior to the activity test, catalyst was treated under flowing N₂ at 300 °C for 1 hr. Pure methanol as the feed was introduced to the preheater which was set at 250 °C. Weight hourly space velocity (WHSV) was set to 5 hr⁻¹ corresponding to the liquid methanol flow rate of 0.16 ml/min.

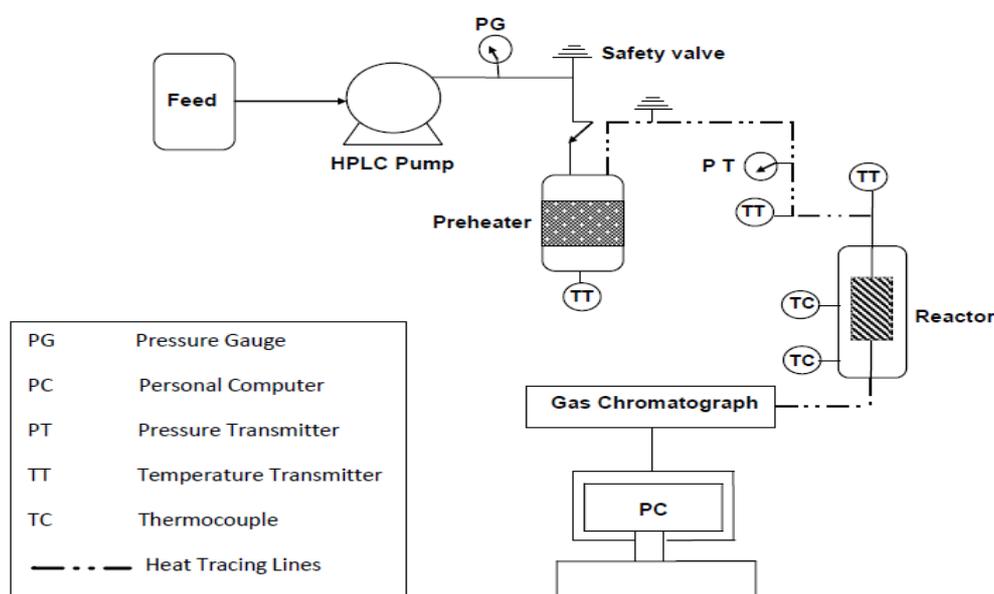


Figure 1

Experimental setup of DME production from methanol

2.5. Product analysis

The products of the reaction leaving the reactor were analyzed using an online gas chromatography (young Lin 6000) equipped with an FID and Plot Q capillary column (30 m length, 0.32 mm ID, 60 micron coating). In order to avoid the condensation of DME, methanol, or water, the output line was heat-traced at a temperature of 200 °C.

3. Results and discussion

3.1. Catalytic characterization

The XRD pattern of MSU-S has been shown in Figure 2. A distinct diffraction peak is illustrated which can be attributed to the (1 0 0) diffraction line characteristic of hexagonal mesostructure.

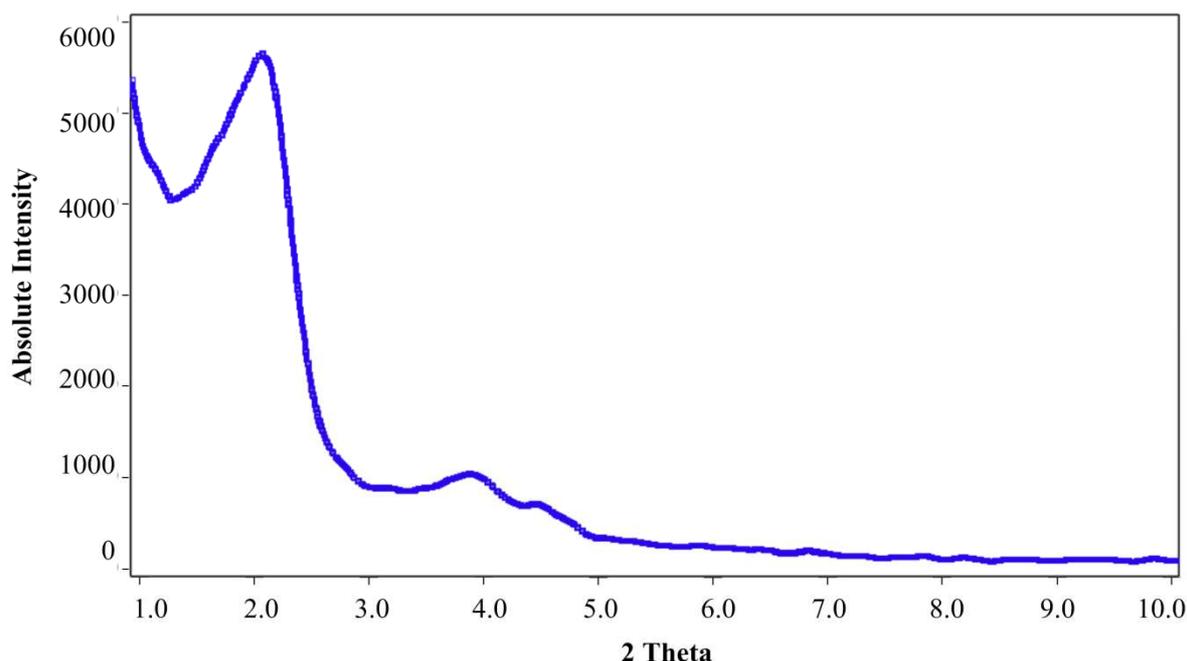
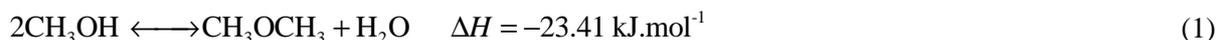


Figure 2
XRD pattern of MSU-S catalyst

3.2. Catalytic activity

Figure 3 shows the trend of methanol conversion over MSU-S catalyst versus reactor temperature. Temperature has been raised from 200 °C to 380 °C at atmospheric pressure.

The methanol dehydration to DME occurs in accordance to Equation 1:



Based on the “Le Chatelier's principle”, in exothermic reactions, the equilibrium conversion decreases by increasing temperature. As it can be seen in Figure 3, equilibrium line has been drawn as a solid line, which shows that equilibrium conversion decreases at higher temperatures; from kinetic point of view, the rate of reaction rises by increasing temperature.

Moreover, the activity of catalyst increases with increasing temperature and reaches a methanol conversion of 59% at 300 °C and approximately the equilibrium conversion at 380 °C. The selectivity of catalyst toward DME is 100% up to 320 °C and decreases gradually and finally falls to 97% at 380 °C. The main byproducts were methane, ethylene, and propylene. Selectivity in methanol dehydration to DME is of great importance and is above 97% for MSU-S catalyst.

Selectivity and conversion were calculated by means of the following equations respectively:

$$\text{DME Selectivity} = \frac{\text{DME moles produced} \times 2}{\text{MEOH moles}(\text{initial amount}) - \text{MEOH moles}(\text{final amount})} \times 100 \quad (2)$$

$$\text{MEOH Conversion} = \frac{\text{MEOH moles}(\text{initial amount}) - \text{MEOH moles}(\text{final amount})}{\text{MEOH moles}(\text{initial amount})} \times 100 \quad (3)$$

Finally, the catalyst life time was investigated for 12 hrs at 380 °C; it showed a stable performance during the mentioned time. MSU-S pore diameter is significantly larger compared to the conventional

catalysts; therefore, coking occurs at a very slow rate on the surface of this catalyst. Coking is the primary reason for the deactivation of solid acid catalysts.

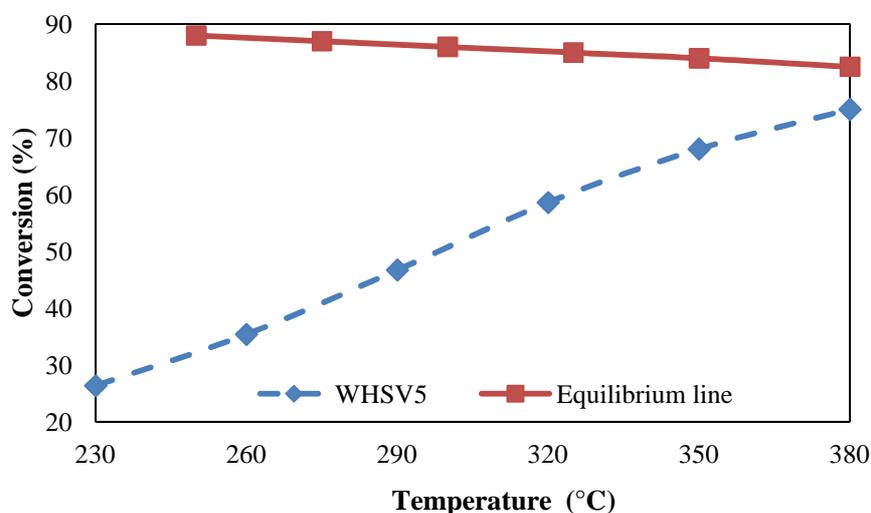


Figure 0

Effect of temperature on methanol conversion

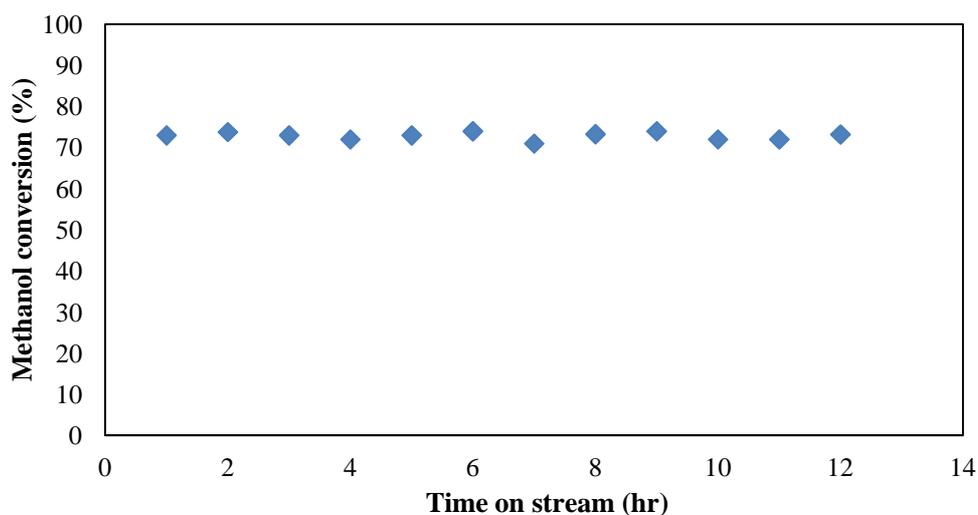


Figure 4

Stability of MSU-S catalyst in 12 hrs at 375 °C

4. Conclusions

MSU-S catalyst with $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio of 55 was synthesized using TPAOH as a structure directing agent and CTAB as a surfactant and was tested for methanol dehydration to DME for the first time in the temperature range of 230 to 380 °C at a WHSV of 5 hr^{-1} . Conversion increased as temperature rose up and approached the equilibrium conversion at 380 °C. In temperature range of 200 °C to 320 °C, selectivity toward DME was 100%. However, selectivity decreased to above 98% at 380 °C. The activity and selectivity of MSU-S catalyst were higher in comparison to Al-MCM-41, which was recently tested for methanol dehydration to DME. It was found that MSU-S could be considered as a potential candidate for future studies.

Nomenclature

CTAB	Hexadecyltrimethylammonium bromide
DME	Dimethyl ether
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High performance liquid chromatography
MAS	Mesoporous alumina silicate
MCM-41	Michigan state university-41
MFI	Mordenite framework inverted
MSU-S	Michigan state university
SAPO	Silicoaluminaphosphate
TPAOH	Tetrapropylammonium hydroxide
WHSV	Weight hourly space velocity
XRD	X-ray diffraction

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