



Effects of Calcination Treatment of Diatomite on Dimethyl Ether Synthesis from Methanol

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ABSTRACT

The synthesis of dimethyl ether via methanol dehydration over diatomite catalysts was investigated. The reactions were carried out in a fixed bed reactor. The effects of calcinations of diatomite on its catalytic performance were studied. Diatomite calcined at 500°C (DM500) gave the higher BET surface than fresh diatomite (DM) due to the loss of ignition. The rate of reaction over DM500 catalyst was lower than fresh DM due to the loss of active sites on the catalyst surface. However, the decrease of basicity of DM500 surface showed the higher selectivity to DME than fresh DM. The DM500 catalyst exhibits better DME yield than fresh DM catalyst, although it can be used as a selective catalyst for DME synthesis from methanol.

1. Introduction

Dimethyl ether (DME) is one of the most promising energy resources because it has better environmental performance and its properties are similar to traditional fuels (West, *et al.*, 2009). Especially, it also has a high cetane number about 55-60 which is significantly alternated to the fossil fuel such as conventional diesel. In Thailand, it can be improved the properties of natural gas by blending it up to 20% into LPG.

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DME can be synthesized via direct synthesis from syngas and methanol dehydration. There are many research focused on the methanol dehydration. There were various types of catalysts such as NaH-ZSM-5 (Vishwanathan, *et al.*, 2004), Au/ZnO/Lz-Y52 (Mpela, *et al.*, 2007), Al-modified Mordenite (Khandan, *et al.*, 2008), and SAPO-11 (Dai, *et al.*, 2011) which could be used for methanol dehydration. It has been reported that there were many parameters affected to DME yield from the methanol dehydration to DME such as the reaction temperature, the methanol flow rate, the catalyst calcination temperature and the acidity of catalysts. It has been concluded that the acid solid catalyst is the most active for catalyzing this reaction; however, the moderate acidity of the surface has been showed the higher yield of DME than the strong acidity catalyst. The zeolite has been selected to be the most active for this reaction. It consists of two main elements which are silica and alumina (Jia, *et al.*, 2008). Their disadvantages bring about unstable catalysts and unexpected products. In this study, the natural porous clay named diatomite has been used as the catalyst due to many acid sites over skeletal form of its surface. Furthermore, it mainly consists of silica and alumina which are similar to natural zeolite. In 2009, the researcher proposed the natural zeolite which was calcined in the temperature range of 500 to 600°C (San, *et al.*, 2009). From this investigation, it has been found that the increasing of its surface area depends on the calcination temperatures. Moreover, there are many types of zeolites, for example Zn/H-ZSM-5 (Yiwen, *et al.*, 2010), aluminophosphate and silico-aluminophosphate (Dai, *et al.*, 2011), and SAPO-34 (Pop and Theodorescu, 2000) which were calcined at the temperature range of 500 to 600°C.

The aim of this research is to study the way to use diatomite as a catalyst for DME synthesis from methanol. It has been focused on the effects of the calcination method and the reaction temperature to the DME yield.

2. Experimental

2.1 Catalysts Preparation

Diatomite was collected from the northern area of Chiangmai Province in Thailand. Diatomite was dried in the oven at 80°C for 24 h, and then it was ground with ball mill and sieved using a 180-mm screen. Afterwards, it was calcined in the oven under air atmosphere at 500°C. The calcined diatomite was labeled as DM500 and diatomite without calcination was called fresh DM.

2.2 Catalyst Characterization

Diatomite microstructure and crystal morphology analysis were determined by scanning electron microscope LEO 1455VP. Thermal gravimetric analysis (TGA) was set to analyze the weight loss of catalysts. Catalysts were placed in alumina cell and heated with the temperature-raising rate of 10°C/min starting from the room temperature to 100°C under nitrogen flow and then the temperature was held at 100°C for 10 minutes. After that, the temperature was increased from 100 to 700 °C with raising rate of 10°C/min under air flow. The signal of TGA was detected by TGA-50H SHIMADZU. X-ray fluorescence analysis (XRF) was used to determine the chemical composition and loss of ignition (LOI) of catalysts to methanol dehydration to dimethyl ether with the parameters to supply in the measurement as 50 kV and 60 mA with rhodium X-ray source to analyze of SRS 340. The catalyst was measured the Brunauer-Emmett-Teller (BET) specific surface area by Microelectronics ASAP2010 physical adsorption apparatus in the condition for N₂ adsorption at -196°C. The X-ray diffraction (XRD) patterns were investigated by Miniflex goniometer fitted with using Ni-filtered CuK α radiation and 2θ continuous-scanning mode and electrical parameters were operated at 30 kV and 15 mA. The acidity of catalysts were measured by the temperature-programmed desorption of ammonia (NH₃-TPD) conducted on BEL JAPAN model BELCAT-B with a thermal conductivity detector (TCD), in the prior experiment, 0.05 g of catalyst was tested under 5% NH₃ and the flow rate of carrier-gas helium at 30 ml/min from 100 to 950°C. And then the basicity of catalysts was measured by the temperature-programmed desorption of carbondioxide (CO₂-TPD) conducted on BEL JAPAN model BELCAT-B with a thermal conductivity detector (TCD), during adsorption and desorption, 0.05 g of catalyst was tested under CO₂ with the flow rate of carrier-gas helium at ml/min from 100 to 800°C.

2.3 Methanol Dehydration

During the methanol dehydration, 0.5 g of activated catalysts (fresh DM and DM500) was loaded into the fixed-bed quartz reactor while methanol was pumped through a syringe peristaltic pump at 0.5 ml/min. The gas condition of MeOH:N₂ was 1:4 (with N₂ flow of 60 ml/min at the atmospheric pressure). The feed was flowed through a peristalsis pump system and changed into the gas state before it was passed through the fixed-bed reactor system using nitrogen gas flow as a carrier gas shown in Figure 1. All products of methanol dehydration

were directly analyzed by on-line gas chromatography with FID and TCD detectors, whereas Porapak T and Molecular Sieve 13X (Shimadzu, GC-14B and Shimadzu, C-R4A) were equipped in these columns. The range of reaction temperature was set between the temperatures of 250°C to 350°C in order to catalyze the reaction.

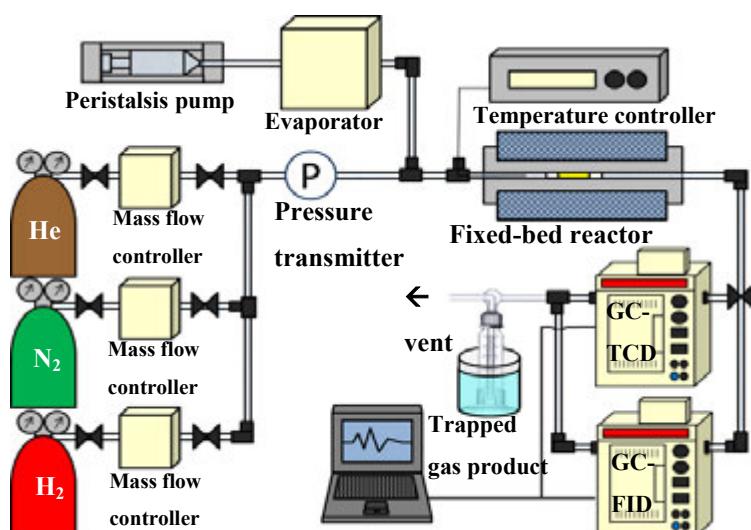


Figure 1: Schematic view of methanol dehydration to dimethyl ether set-up

3. Results and Discussion

Table 1: The physical properties of DM and DM500 catalysts

Catalyst	Composition (% wt)					Si/Al	S_{BET} (m^2/g)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Other	LOI		
Fresh DM	80	9.6	2.5	1.8	6.14	8.3	25
DM500	82	10	4.2	2.5	0.72	8.1	37

Denote: LOI is loss of ignition and S_{BET} is BET surface area

3.1 The effects of calcination treatment on the physical

The physical properties of catalysts are summarized in Table 1, the results of chemical composition of fresh DM and DM500 by XRF shown that the calcined temperature could not influence the chemical composition for metal compound and their surface areas, but it could only decrease the organic compounds (as LOI composition in XRF data) in their compositions. The fresh DM consisted of the organic compounds about 6.14% while the DM500 had only about 0.72%. The LOI from XRF data of DM500 was followed by TGA data in Figure 2, which there was no weight loss, while weight loss about 17% was present in fresh DM. The

BET surface area of fresh DM was increased from 25 to 37 m²/g (about 50% of enhancement as compared with fresh DM) by calcined temperature treatment at 500°C. On the other hands, there was no effect on silica alumina ratio (8.1-8.3).

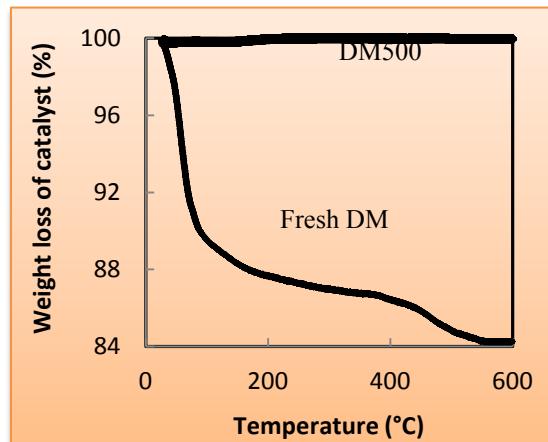


Figure 2: TGA data of fresh DM and DM500

According to the research data of San, et al., (San, et al., 2009) for characterizing composition and phases in Turkey diatomite, the XRD pattern is presented in all phases (quartz, albite, tridymite, orthoclase, microcline, aluminium silicate and magnesium silicate) which are similar to Chiangmai diatomite for this research. In amorphous phase of both catalysts; aluminium silicate, magnesium silicate and microcline are the main phases in this skeletal form. However, a significant crystalline phase is silica in the great majority of composition of quartz phase as shown in Figure 5. The phases of these catalysts were not changed in order to increase the calcinations temperature to 500°C.

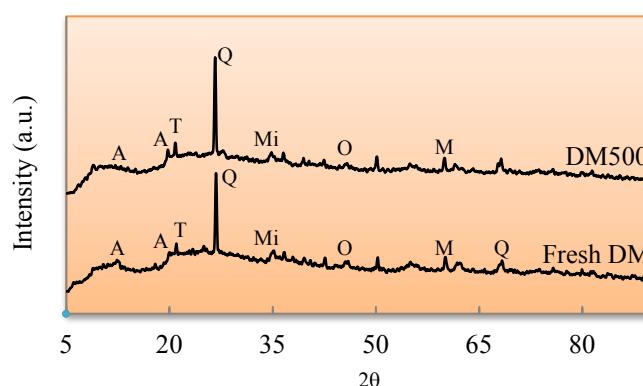


Figure 3: XRD patterns of fresh DM and DM500; A = Aluminium silicate, M = Magnesium silicate, Mi = Microline, O = Orthoclase, Q = Quartz and T = Tridymite

In the process of calcinations treatment at 500°C, there was no effect on morphology of

DM as shown in Figure 4 which illustrated the scanning electron micrographs of fresh DM and DM500. The shape of diatomite was not deformed at the temperature of 500°C since the main phase still had the open pores of skeletal-shaped diatomite. Furthermore, the hollow and porous structure of these catalysts was fully filled with the agglomerates of cracked structure and the unidentified particles, such as pre- and post-calcination treatments at this temperature. The morphology of both catalysts was similar to the data of (Chaisena and Rangsriwatananon, 2005) that there was no deformation in diatomite at the high-temperature calcination (1100°C, 5 h).

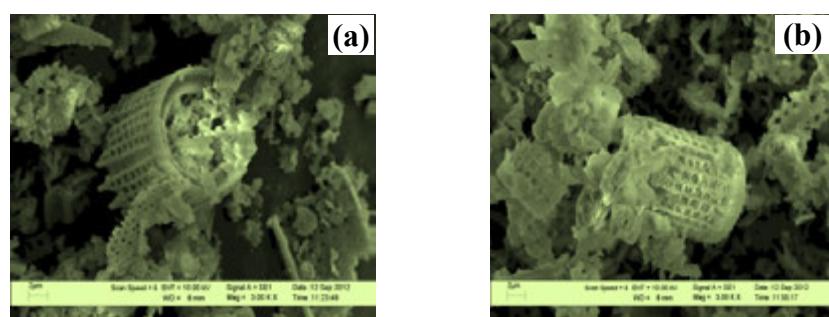


Figure 4: Scanning electron micrograph of diatomite with 1,000 magnification; (a) Fresh DM and (b) DM500

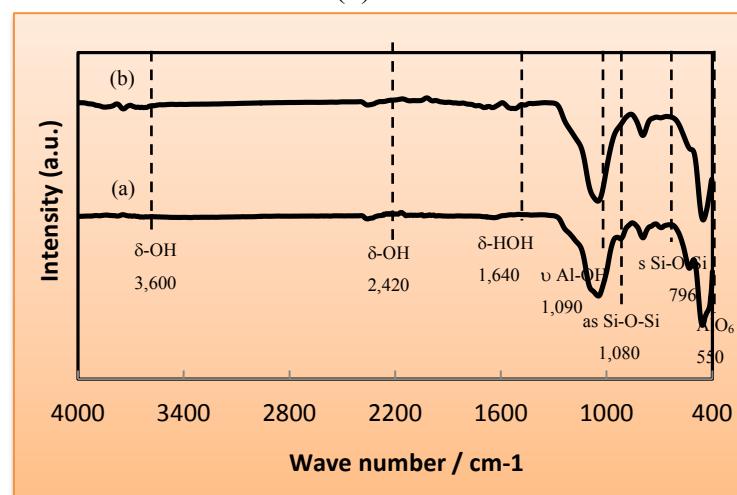


Figure 5: FT-IR spectra of Fresh DM and DM500; (a) Fresh DM and (b) DM500

By using this treatment, neither did the phases and the morphology of diatomite have any interaction, nor were the functional groups arranged in diatomite's structure influenced. Based on the FT-IR spectra from the identification of (Crisan, *et al.*, 2006) there was the group of siloxane (Si-O-Si) at 1,080 cm^{-1} connected to the aluminium hydroxide group at 1,090 cm^{-1} , and silicon in the structure was bonded to hydroxyl group (-OH) to form the silanol group (S-OH) at 2,420 and 3,600 cm^{-1} . The observed FT-IR spectra of fresh DM and DM500 were illustrated in Figure 5.

3.2 The effects of calcination treatment on the activity of methanol dehydration to DME over diatomite catalysts

According to Table 1, the amounts of oxide compounds and LOI in fresh DM were changed by the calcination treatment at 500°C. However, this treatment had no effect on the silica-alumina ratio. For this stable ratio, there was no difference between the activity of fresh DM and that of DM500 as shown in Figure 6, suggesting that the activity was slightly influenced by calcination treatment at 500°C to methanol conversion rate via methanol dehydration to DME. On the contrary, the uncalcined diatomite exhibited DME showed lower selectivity than calcined diatomite at 500°C as seen from Figure 7.

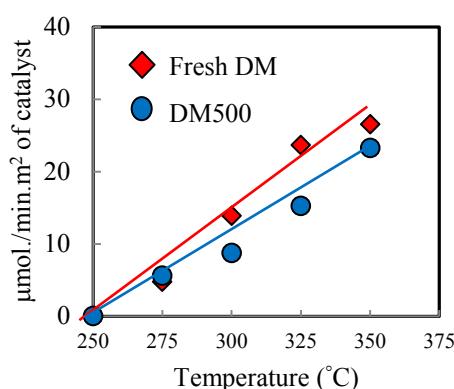


Figure 6: The effects of calcination treatment of diatomite on methanol conversion rate via methanol dehydration over fresh DM and DM500 catalysts at the reaction temperature from 250 to 350°C

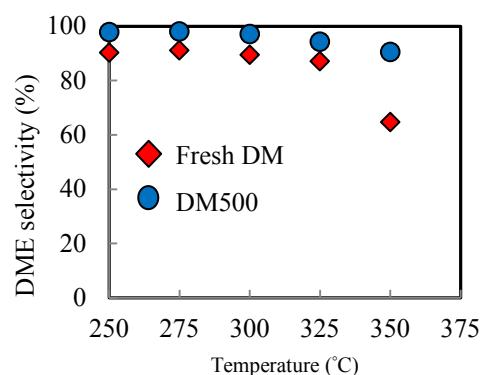


Figure 7: The effects of calcination treatment of diatomite on dimethyl ether selectivity via methanol dehydration over fresh DM and DM500 catalysts at the reaction temperature from 250 to 350°C

DME was selected to be the main product for both of catalysts whereas, for fresh DM, there were directly-gained DME and rapidly-increasable unexpected product as seen in Figure 8 (such as formaldehyde via methanol dehydrogenation) and depended on the reaction

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temperature (250 to 350°C). The calcination treatment of catalyst at 500°C could not increase the by-product distribution because the DME selectivity, as it is seen in Figure 7, was kept to its 90% trend-line along the reaction temperature of 250 to 350°C. For catalytic characterizations – such as XRD, SEM and FT-IR, it could suggest that the methanol conversion rate and the selectivity of DME were independent from these characterizations. On the other hand, the increased surface area of diatomite after calcinations at 500°C had the influence in decreasing the acid sites per area of diatomite to lower than that of uncalcined diatomite as shown in Table 2, which was also confirmed with the decreased methanol conversion rate of DM500. By considering the acidity from Table 2 by NH₃-TPD method, it showed that DM500 had the greater number of acid sites per area than fresh DM. Hence, DME selectivity of DM500 less decreased than that of fresh DM. Nonetheless, the CO₂-TPD data in Table 3 could significantly support the unexpected products especially form methanol dehydration. The higher amount of basic sites per area of fresh DM than that of DM500 revealed that fresh DM should enhance the competitive reaction with increasing the reaction temperature.

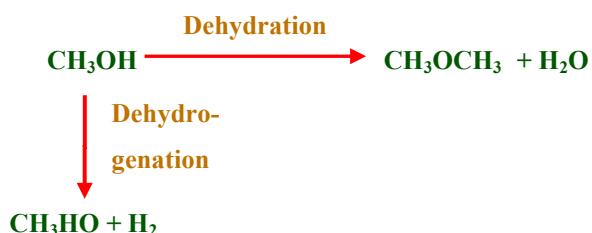


Figure 8: Methanol dehydration to dimethyl ether and methanol dehydrogenation to formaldehyde reaction pathway

Table 2: The amount of acid sites of catalysts from NH₃-TPD method

Catalysts	Weak acid at 190°C (μmol/m ²)	Strong acid at 630°C (μmol/m ²)	Total acidity (μmol/m ²)
Fresh DM	3.560	40.320	43.880
DM 500	3.162	29.351	32.514

Table 3: The amount of basic sites of catalysts from CO₂-TPD method

Catalysts	Weak base at 160°C (μmol/m ²)	Strong base at 630°C (μmol/m ²)	Total basicity (μmol/m ²)
Fresh DM	13.560	128.560	142.120
DM 500	8.297	77.243	85.541

From the calcination treatment result, it could suggest that DM500 was a more suitable catalyst than fresh DM to synthesize DME via methanol dehydration, though it still have lower methanol conversion rate than fresh DM.

4. Conclusion

It can be concluded that the calcination treatment had no effect on characterizations such as the ratio of silica and alumina, phases, morphology and functional groups in both diatomite catalysts. The calcination treatment at 500°C could decrease the LOI to lower than 1%, resulting in increasing of BET surface with no weight loss of diatomite.

In the catalytic activity study, the calcination at 500°C of diatomite had effects on higher acid sites per area, lower basic sites per area, and lower organic compound in its structure than fresh DM. DM500 exhibited high DME selectivity – over 90% – at the reaction temperature from 250 to 300°C while fresh DM had DME selectivity below 90% with many directly contributed products depending on the reaction temperature. Furthermore, it can be concluded that calcination treatment at 500°C also plays one important role in the effect of diatomite catalysts on synthesized dimethyl ether via methanol dehydration.

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