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Methanol Dehydration to Dimethyl Ether
over Kaolinite-supported TiO₂ CatalystsImran ROSADI^{*1}, Arthit NERAMITTAGAPONG^{*1*2*3}, Pakpoom ATHIKAPHAN^{*1},
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The present work aims to study the catalytic performance of kaolinite (KN)-supported TiO₂ in the production of dimethyl ether (DME) from methanol. KN was doped with 0, 3, 5, 10, and 15 wt% Ti composite particles via the sol-gel method. The performance of the TiO₂/KN catalysts were then tested in a fixed-bed reactor having a temperature in the range 200-350 °C under atmospheric pressure. The molar ratio of methanol to nitrogen, total gas flow rate, and weight hourly space velocity (WHSV) were set to 1:4, 60 mL/min at standard temperature and pressure, and 2.054 h⁻¹, respectively. The catalysts were characterized using scanning electron microscopy, the Brunauer-Emmett-Teller method, X-ray diffraction, and temperature-programmed desorption of NH₃. The final products were analyzed using gas chromatography. An increase in Ti loading yielded a higher methanol conversion rate owing to the increase in the number of acid sites on the catalyst surface. The highest methanol conversion rate of 79% was reported for TiO₂/KN (Ti=15%) at 350 °C. However, TiO₂/KN (Ti=15%) exhibited low selectivity to DME owing to the decomposition of DME to CH₄ and CO₂. Our results indicate the optimum Ti loading to be TiO₂/KN (Ti=10%), which resulted in a catalyst that was active at 250 °C and showed good selectivity to DME.

Key Words

Kaolinite, TiO₂, Renewable energy, Methanol dehydration, Dimethyl ether

1. Introduction

Currently, the use of fossil fuels poses a serious problem. This is because although the demand for energy has increased globally, fossil energy resources have decreased. Moreover, the combustion of fossil fuels leads to serious environmental issues, such as air pollution. Therefore, several alternative fuels have been proposed, such as dimethyl ether (DME; C₂H₆O). DME is a promising fuel because it is renewable and environmentally friendly. Additionally, it has a high cetane number in the range

55–66 and can be blended with LPG, diesel, and biodiesel¹⁾. DME can be produced by the dehydration of methanol (CH₃OH) on solid acid catalysts, such as diatomite, zeolite, and γ-Al₂O₃^{2) ~ 8)}. These catalysts contain silica and alumina that act as acid sites over which methanol can be dehydrated. Interestingly, solid acid catalysts have also been developed from natural clay, for example, kaolinite. Kaolinite has high silica and alumina contents²⁾ and dehydration of methanol to DME over pure kaolinite has been reported with a methanol conversion rate of more than 80% at a temperature of 400 °C³⁾. However, such high-temperature synthesis of DME leads to high production costs as well. Moreover, our previous work showed that the dehydration of methanol to DME over pure kaolinite is problematic because of the formation of hydrocarbons and coke³⁾. Note that CH₄ and CO₂, which are the by-products of DME synthesis via methanol dehydration, are produced at high temperatures⁴⁾. In addition, one of the main drawbacks of kaolinite is its low surface area of approximately 11 m²/g⁵⁾. In a previous study, dehydration of methanol to DME over

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Co/kaolinite was achieved with a methanol conversion rate of 81.7% and DME selectivity of 79% at a temperature of 350 °C. It should be noted that although Co/kaolinite exhibits high performance during the dehydration of methanol to DME, it requires a very high temperature⁶⁾. To overcome this problem, it has been proposed that the surface area of kaolinite be increased by doping kaolinite with TiO₂⁵⁾. Furthermore, Ladera et al. used TiO₂-supported heteropoly acid catalysts to facilitate the dehydration of methanol to DME at a low temperature of 180 °C and reported a methanol conversion rate of approximately 80%^{7,8)}.

In the present work, we aim to study the effect of TiO₂-loaded kaolinite on the synthesis of DME from methanol via the sol-gel method.

2. Methodology

2.1 Catalyst preparation

The kaolinite used in this study was acquired from Ranong, Thailand. It was dried in an oven at 80 °C for 24 h and sieved using a 170-mesh screen. Subsequently, the pure kaolinite was calcined at 600 °C for 4 h. Following this, the calcined kaolinite powder was refluxed with 1 M sulfuric acid in a three-necked flask at 100 °C for 2 h. Next, it was washed with deionized water until a pH of 7 was reached and dried at 100 °C for 2 h. This sample was labeled KN and used as the support for the catalyst.

TiO₂/KN catalysts with different Ti loadings of 3, 5, 10, and 15 wt% were prepared using the sol-gel method. Note that the weight percentage of TiO₂ was calculated based on the weight percentage of Ti in the KN support. To prepare TiO₂/KN (Ti=3%) catalyst, TiCl₄ (Merck, 99.0%) was slowly added to ethanol (C₂H₅OH) solution (ACI Labscan, 99.99%) in a glass beaker until the TiCl₄:C₂H₅OH ratio reached 1:30. During this process, the solution was stirred continuously at a constant rate for 30 min at room temperature. Next, KN was added and the mixture was stirred continuously for 30 min. Then, NH₄OH solution (QReC, 28.0%) was slowly added to the mixture until a pH of 7 was reached. Thereafter, the sample was sonicated in an ultrasonic bath having temperature in the range 35–40 °C for 2 h, following which it was kept at room temperature for 24 h. Subsequently, the gel was washed with deionized water and dried in an oven at 100 °C for 9 h. Finally, the gel was calcined in a muffle furnace at 600 °C for 4 h. Note that the TiO₂/KN (Ti=5%), TiO₂/KN (Ti=10%), and TiO₂/KN (Ti=15%) catalysts were prepared in the same manner.

2.2 Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface area of the catalysts was characterized using Microelectronics

ASAP2010. Field emission scanning electron microscopy (FE-SEM; FEI Helios NanoLab G3 CX) was used to determine the morphology of the catalysts. The phase structure of the catalysts was analyzed using X-ray diffraction spectroscopy (XRD; PANalytical EMPYREAN, United Kingdom). The acidic properties of the catalyst surfaces were determined using temperature-programmed desorption (TPD) of ammonia (NH₃-TPD; Chemisorption Analyzer BELCAT II, Japan). These experiments were performed at a temperature in the range 393–1,173 K. Prior to the NH₃-TPD experiments, the sample (500 mg) was outgassed at 773 K in a flow of dry He (30 mL/min) for 1 h. Subsequently, the sample was cooled to 393 K and saturated for approximately 30 min in an NH₃ flow (30 mL/min). The sample was then purged in a He flow until a constant baseline level was attained. Finally, desorption was carried out at a linear heating rate of 10 K/min in a He flow.

2.3 Methanol dehydration

Methanol dehydration over TiO₂/KN (Ti=3%), TiO₂/KN (Ti=5%), TiO₂/KN (Ti=10%), and TiO₂/KN (Ti=15%) catalysts were tested in a fixed-bed reactor at atmospheric pressure and at temperatures 200, 250, 300, and 350 °C. Methanol was first pumped into the evaporator and then mixed with N₂ gas in 1:4 molar ratio. The gas feed flow rate and weight hourly space velocity (WHSV) were fixed at 60 mL/min and 2.054 h⁻¹, respectively. The reactants and products were analyzed via gas chromatography (Shimadzu, GC-14B, Japan) using a flame ionization detector (FID) and a thermal conductivity detector (TCD). The conversion rate of methanol and final product selectivity were calculated using the following equations:

$$\% \text{Conversion} = \frac{\sum(n_i \times c_i)}{M + \sum(n_i \times c_i)} \times 100 \quad (1)$$

$$\% \text{Selectivity} = \frac{(n_i \times c_i)}{\sum(n_i \times c_i)} \times 100, \quad (2)$$

where n_i is the number of moles of product i in the reaction, c_i is the number of C atoms in product i , and M is the number of moles of methanol at the outlet.

3. Results and Discussion

The XRD patterns of the catalysts are shown in Fig. 1. The peaks indicate the presence of quartz that appear at 2 theta of 26.7°, 36.6°, 39.5°, 40.3°, 42.5°, 45.4°, and 50.2°, which is in accordance with the quartz standard presented by Khalifah *et al.*⁹⁾. It can be clearly seen that the phase structures of all the catalysts are nearly the same. This is probably because of the low Ti content of kaolinite and small size of the TiO₂ particles. Note that the diffraction peak of kaolinite is higher than that of TiO₂. In this respect,

Fig. 1 XRD patterns of different catalysts: (a) KN, (b) TiO_2/KN (Ti=3%), (c) TiO_2/KN (Ti=5%), (d) TiO_2/KN (Ti=10%), and (e) TiO_2/KN (Ti=15%)

our XRD data are similar to those reported by Ji *et al.*, where the kaolinite was treated with 33.33% Ti composite particles¹⁰. However, as shown in Fig. 2, all the catalysts exhibit different morphologies and elemental compositions before and after the treatment. The morphology of kaolinite was deformed following the treatment with Ti. Note that the Ti particles in kaolinite have a stick-like structure. The kaolinite was loose and the Ti composite increased after the treatment. This result is similar to that of Ji *et al.*, who also found that the morphology of kaolinite changed following the treatment with TiO_2 ¹⁰. In addition, the structure of Ti on kaolinite was confirmed by FE-SEM, as shown in Fig. 3.

The surface area of kaolinite was found to increase following the treatment with Ti (see Table 1) because of the creation of new pores. Elemental mapping of TiO_2/KN (Ti=10%) confirmed that fine TiO_2 particles were dispersed on the kaolinite surface, as shown in Fig. 3. However, as shown in Table 1, the surface area of kaolinite decreased when the Ti loading exceeded 10% owing to the TiO_2 particles accumulating on the kaolinite surface in this case. In addition, all the samples were characterized using NH_3 -TPD to analyze the acidity of the catalysts. The acidity of the catalysts did not change significantly and only increased slightly following the treatment with Ti, as shown in Table 1. However, the Ti doping changed the type of acid groups found on the catalysts, as shown in Fig. 4. Pure kaolinite has three types of acid groups: weak (125–500 °C), medium (500–690 °C), and strong (690–850 °C); whereas, kaolinite treated with Ti has only two types of acid groups: weak (125–500 °C) and strong (500–850 °C). The increase in the number of strong acid sites following the Ti treatment was

significant. These data further indicate that increasing the surface area of kaolinite by treating with Ti not only increases its acidity but also changes the type of acid sites available on the catalysts.

We investigated the dehydration of methanol to DME over kaolinite catalysts with different TiO_2 loadings and the results are shown in Fig. 5. We observe that the methanol conversion rate and DME selectivity exhibit different trends. The methanol conversion rate increased with an increase in the reaction temperature; however, selectivity to DME decreased with temperature. Methanol dehydration to DME over pure kaolinite yielded a methanol conversion rate of 72% and DME selectivity of 86% at a temperature of 350 °C. A similar result has been reported previously, namely, DME synthesis via methanol dehydration over pure kaolinite requires high temperatures to achieve high methanol conversion rates³.

In contrast, the highest methanol conversion rate of 79% with a low DME selectivity of 40% were obtained for TiO_2/KN (Ti=15%) at 350 °C. The gas chromatography results presented in Figs. 6 and 7 show the presence of CO_2 and CH_4 peaks in the TCD data at retention times of 5.082 and 8.632 min, respectively; whereas the CH_4 peak in the FID data was detected at a retention time of 8.298 min. Herrera *et al.* reported the decomposition of DME over a Ta/ TiO_2 catalyst in the temperature range 250–450 °C either to CH_4 , H_2 , and CO or to CH_4 and CO_2 ¹¹. This indicates that DME can decompose over TiO_2 catalysts to form CH_4 and CO_2 . Thus, the decrease in selectivity to DME observed in this work may be due to the formation of CH_4 and CO_2 from DME decomposition.

Fig. 2 FE-SEM images of different catalysts: (a) KN, (b) TiO₂/KN (Ti=3%), (c) TiO₂/KN (Ti=5%), (d) TiO₂/KN (Ti=10%), and (e) TiO₂/KN (Ti=15%)

Fig. 3 Elemental mapping of different catalysts: (a) KN, (b) TiO₂/KN (Ti=3%), (c) TiO₂/KN (Ti=5%), (d) TiO₂/KN (Ti=10%), and (e) TiO₂/KN (Ti=15%)

Table 1 Physical properties of pure kaolinite and kaolinite-supported Ti catalysts

Catalyst	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	*Acidity (μmol/g)
KN	16	0.04	1195
TiO ₂ /KN (Ti=3%)	41	0.07	1196
TiO ₂ /KN (Ti=5%)	42	0.09	1203
TiO ₂ /KN (Ti=10%)	43	0.09	1205
TiO ₂ /KN (Ti=15%)	36	0.08	1204

Note: S_{BET} is the BET surface area of the catalysts; (*) analyzed using the NH₃-TPD method.

Fig. 4 NH₃-TPD patterns of pure kaolinite and kaolinite-supported TiO₂ catalysts

Fig. 5 (a) Methanol conversion, (b) DME selectivity

As shown in Fig. 5, pure kaolinite and TiO₂/KN (Ti=3%) were not active at a reaction temperature of 200 °C. We also observe that the KN catalysts with different TiO₂ contents exhibited methanol conversion rates in the range 5–62% at a reaction temperature of 250 °C. However, it should be noted that although TiO₂/KN (Ti=15%) exhibited a high methanol conversion rate, it had low DME selectivity at this temperature. Therefore, we can conclude that the TiO₂/KN (Ti=10%) catalyst is most suitable for DME production at a reaction temperature of 250 °C because it exhibits a methanol conversion rate of 47% and DME selectivity of 92%. This result confirms that the increase in the number of acid sites following Ti loading, as shown in

Table 1 and Fig. 4, significantly increased the activity of the catalysts in the temperature range 200–300 °C. However, the activity of the catalysts decreased at high temperatures (e.g., 350 °C), which might be due to the formation of coke from further dehydration of the products on the surface of the catalysts. Note TiO₂/KN (Ti=15%) exhibited a high methanol conversion rate at 350 °C, which might be due to the conversion of DME to CH₄ and CO₂ during the reaction. In contrast, TiO₂/KN (Ti=10%) showed a methanol conversion rate of 63% and DME selectivity of 84% at 300 °C. It also exhibited good performance in methanol conversion and DME selectivity in the temperature range 200–300 °C. Thus, TiO₂/KN (Ti=10%) would be a good candidate for an active

Fig. 6 TCD data from gas chromatography for TiO_2/KN (Ti=10%) catalyst at 350°C Fig. 7 FID data from gas chromatography for TiO_2/KN (Ti=10%) catalyst at 350°C

and selective catalyst in this reaction temperature range.

The gas chromatography results of methanol dehydration to DME over TiO_2/KN (Ti=10%) are shown in Figs. 6 to 9. The corresponding results at 200°C are shown in Figs. 8 and 9. We observe that the TCD data in Fig. 8 shows N_2 , DME ($\text{C}_2\text{H}_6\text{O}$), H_2O , and methanol (CH_3OH) peaks at retention times 5.990, 18.198, 258.32, and 29.698 min, respectively. The FID data in Fig. 9 shows DME and methanol peaks at retention times 18.357 and 29.832 min, respectively. In addition, the results of methanol dehydration to DME at 350°C are shown in Figs. 6 and 7. In Fig. 6, the TCD data exhibits CO_2 , N_2 , CH_4 , $\text{C}_2\text{H}_6\text{O}$, H_2O , and CH_3OH peaks at retention times 5.082, 5.965, 8.632, 17.732, 24.832, and 30.432 min, respectively; whereas, the FID data in Fig. 7 shows CH_4 , $\text{C}_2\text{H}_6\text{O}$, and CH_3OH peaks at retention times 8.298, 17.865, and 30.598 min, respectively.

According to these results, it can be concluded

that the synthesis of DME via methanol dehydration over kaolinite treated with TiO_2 (having different Ti loadings of 5, 10, and 15 wt%) consists of two major reactions. The first reaction is methanol dehydration and the second is product decomposition, as shown by Eqs. (3) and (4), respectively. The decomposition reaction for TiO_2/KN (Ti=5%) and TiO_2/KN (Ti=10%) occurs in the temperature range $250\text{--}350^\circ\text{C}$, while that for TiO_2/KN (Ti=15%) occurs in the temperature range $200\text{--}350^\circ\text{C}$. Note that pure kaolinite and TiO_2/KN (Ti=3%) did not exhibit any decomposition reaction because these catalysts are not active in the concerned temperature range.

In Table 2, we compare the results of DME synthesis

Fig. 8 TCD data from gas chromatography for TiO_2/KN (Ti=10%) catalyst at 200 °C Fig. 9 FID data from gas chromatography for TiO_2/KN (Ti=10%) catalyst at 200 °C

Table 2 Methanol dehydration to DME over different catalysts

Catalyst	Method	WHSV (h^{-1})	Pressure (MPa)	Temperature (°C)	Methanol Conversion (%)	DME Selectivity (%)	Ref.
TiO_2/KN (Ti=10%)	sol-gel	2.054	0.1	250	47	92	This work
Diatomite	strong acid treatment	2.054	0.1	250	~10	~95	12)
$\gamma\text{-Al}_2\text{O}_3$	co-precipitation	20	0.2	250	33.8	99.9	13)
$\gamma\text{-Al}_2\text{O}_3$	commercial catalyst supplied by Aldrich	1.3	0.1	250	34	100	14)
$\text{CuO-Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	impregnation	1.3	0.1	250	34	100	14)

via methanol dehydration over various catalysts using different methods. We observe that at 250 °C, the TiO_2/KN (Ti=10%) catalyst used in this work has a higher methanol conversion rate compared to other catalysts as well as good selectivity to DME.

4. Conclusions

In the present study, we showed that loading kaolinite with TiO_2 can significantly change the physical and chemical properties of the catalyst. The presence of TiO_2 on the surface of kaolinite increased the number of acid sites, which in turn increased the methanol conversion rate. However, very high TiO_2 loadings resulted in low selectivity to DME due to the decomposition of DME to

methane and carbon dioxide. The optimum loading of TiO₂ on kaolinite to produce DME via methanol dehydration was found to be TiO₂/KN (Ti=10%) for temperatures in the range 200-350 °C. Thus, TiO₂/KN (Ti=10%) is a suitable catalyst for DME production as it exhibits good activity and product selectivity.

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