Effect of HCl Loading and Ethanol Concentration over HCl-Activated Clay Catalysts for Ethanol Dehydration to Ethylene

Chadaporn Krutpijit and Bunjerd Jongsomjit*

Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, THAILAND

Abstract: Montmorillonite clay (MMT) is one of materials that can be “green material” due to its environmental safety. In this work, acid-activated MMT catalysts were prepared for the dehydration reaction of ethanol. To be the green process, the reaction with bioethanol was also studied. Ethanol concentrations in feed were varied in the range of 10-99.95 wt%. Moreover, the concentrations of hydrochloric acid activated MMT were investigated in range of 0.05-4 M. From the experiment, it reveals that different acid concentrations to activate MMT affect the catalytic activity of catalysts. The 0.3 M of HCl activated MMT exhibits the highest activity (under the best condition of 30 ml HCl aging for 1 h) with the Si/Al ratio of 7.4. It can reach the ethanol conversion and ethylene selectivity up to 95% and 98% at reaction temperature of 400°C, respectively. For the several ethanol feed concentrations, it does not remarkably affect in ethanol conversion. However, it has some different effect on ethylene selectivity between lower and higher reaction temperatures. It was found that at lower temperature reaction, ethylene selectivity is high due to the behavior of water in feed. In addition, the 0.3 M-MMT can be carried out under the hydrothermal effect.

Key words: ethanol, catalytic dehydration, montmorillonite clay, hydrochloric acid, acid activation, diethyl ether, ethylene

1 INTRODUCTION

Most petrochemical products such as acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride, vinyl acetate can be produced from ethylene. Moreover, ethylene also can be used as feedstock in polymerization reaction to the formation of polyethylene, polyvinyl chloride and polystyrene1. Currently, ethylene has been commercially produced by thermal cracking reaction of petroleum or natural gas feedstock. The disadvantages of this process are the limitation of natural gas feedstock and highly energy consumption due to high temperature operation (ca. 750-900°C) due to endothermic operation and high CO2 emission2, 3.

Nowadays, the CO2 emission problem in chemical industries is important and should be reduced. Therefore, the biochemical such as bio-ethanol may facilitate the reduction of CO2 emission in the petroleum industries4. In the present study, ethylene formation via catalytic dehydration of ethanol was investigated. This alternative way is the merit to produce green ethylene because ethanol is a chemical obtained from renewable feedstock (biomass such as molasses and starch) via fermentation and catalytic dehydration of ethanol can be operated at low temperature.

In the catalytic dehydration of ethanol, two reactions can occur in parallel reactions as follow2, 5, 6:

$$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \Delta H = +44.9 \text{ kJ/mol}$$ (I)

$$2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} \quad \Delta H = -25.1 \text{ kJ/mol}$$ (II)

The first reaction (I) is endothermic reaction, which main product is ethylene. The second reaction (II) can be operated at lower temperature due to exothermic reaction to obtain diethyl ether. Another reaction from ethanol via dehydrogenation reaction can also produce acetaldehyde as third reaction (III) below2, 7:

$$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2 \quad \Delta H = +82.5 \text{ kJ/mol}$$ (III)

It is well known that solid acid catalysts have been widely investigated in catalytic dehydration of ethanol2, 4, 8-10. The
most common solid acid catalysts are alumina$^{2,11}$, silica$^{12}$, silica-alumina$^{13,14}$, zeolite$^{15,16}$ and titania$^{17}$. Not only these catalysts were studied, but the montmorillonite (MMT) was also selected to study for this reaction due to its acidic nature and it can be used as Brønsted acid catalyst, which is better for the catalytic dehydration of ethanol. The 2:1 smectite group of dioctahedral or trioctahedral is considered as green material due to its environmental safety. It is also cheap, easy modification and availability and high surface area$^{17,18}$. Based on previous works, MMT is used in many applications including isomerization α-pinene$^{19}$, alkylation of toluene$^{20}$, esterification of lauric acid$^{21}$ and dehydration n-butanol$^{22}$. In addition, MMT was also activated with heteropolyacid which was investigated by Bokade and Yadav$^{23}$. This research represented the active catalyst in bioethanol dehydration, where the dodecatungestophosphoric acid (DTPA) was supported on MMT. It increased ethylene selectivity. However, it is high-cost operation due to the preparation of catalysts. In our previous study in catalytic ethanol dehydration over different acid-activated montmorillonite clays$^{24}$, we have developed a high performance of MMT with acid activation using hydrochloric acid (HCl). It was found that the activation with hydrochloric acid led to enhance catalytic activity of ethanol dehydration having only slight deactivation after 72 h with less carbon deposition.

In this study, we further investigate the effect of HCl loading on MMT to obtain the best condition of prepared catalysts and also investigated the catalytic performance of obtained catalyst under effect of water in the ethanol feed condition in order to find the appropriate condition of bioethanol dehydration reaction.

2 EXPERIMENTAL

2.1 Materials

The commercial Al-pillared MMT clay and 37% hydrochloric acid, which was used to activate the MMT clay were obtained from Sigma-Aldrich Chemical Company, Inc. 99.95% Absolute ethanol was purchased from Merck. Deionised water was used to prepare a range of ethanol concentrations (10, 30, 50 80 wt% of ethanol)

2.2 Preparation of acid-activated MMT

The catalyst samples were prepared with acid-activation by stirring 1 g of MMT in hydrochloric acid (HCl) solution with volume of 30 ml using concentrations of 0.05 M, 0.1 M, 0.3 M, 0.5 M, 0.7 M, 1 M, 2 M and 4 M for 1 h. The HCl-activated MMT catalysts were kept in an oven at 125°C for 21 h. Then, all samples were removed Cl by washing with DI water until neutral and dried overnight at 110°C. The catalyst samples were denoted as x M-MMT (x means the concentration of hydrochloric acid for the activation of MMT catalyst).

2.3 Characterization

The characterization techniques of catalysts include XRD, N$_2$ physisorption, FTIR, NH$_3$-TPD, SEM/EDX and TGA. The details are as follows;

2.3.1 Powder X-ray diffraction (XRD)

XRD patterns of catalysts were obtained by X-ray diffractometer (Bruker AXS Model D8 Discover) with CuK$_\alpha$ radiation source (λ = 1.54439 Å) and Ni filter. The catalysts were scanned in the range of 20 = 3 to 45° with a resolution of 0.02°.

2.3.2 N$_2$ physisorption

N$_2$ physisorption was used to determine the specific surface area, pore volume and pore size diameter of prepared catalysts using Micromeritics Chemisorb 2750 Pulse chemisorption system instrument. The gas adsorption and desorption isotherms were conducted at liquid nitrogen temperature (−196°C) and calculated using the Brunauer, Emmett, and Teller (BET) isotherm equation.

2.3.3 Fourier transform infrared spectroscopy (FTIR)

The IR spectroscopy was used to identify specific structural characteristics of the chemical group from the vibration properties by Nicolet 6700 FTIR spectrometer in the range of 400 to 4000 cm$^{-1}$.

2.3.4 Temperature-programmed desorption of ammonia (NH$_3$-TPD)

The acid properties of samples were determined using Micromeritics chemisorb 2750 pulse chemisorption system. The catalyst sample was packed in a U-tube glass with quartz wool and pretreated under helium flow at 500°C for 1 h. Then, the catalyst sample was saturated with 15% of NH$_3$/He at 40°C for 30 min. After saturation, the physisorbed ammonia was desorbed under helium gas flow. Then, the chemisorbed ammonia was removed from active sites from temperature of 40°C to 500°C at heating rate of 10°C/min. Amount of ammonia is related to acidity of catalyst.

2.3.5 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Hitashi mode S-3400N was used to determine the morphology of catalysts with the accelerating voltage of 30 kV and magnification ranging from 1,000 to 10,000 and the resolution of 3 nm. The SEM was carried out using the secondary scattering electron (SE) mode. The sample of SEM observation was conductive to prevent charging by coating with platinum under the ion sputtering device. EDX was performed using Apollo X Silicon Drift Detector Series by EDAX to determine the elemental distribution and composition over different catalysts.

2.3.6 Thermal gravimetric analysis (TGA)

TGA was performed using the thermal gravimetric SDT analyzer model Q600. The sample was carried out under a heating rate of 10 °C min$^{-1}$ from 30 to 1000 °C to investi-
gate the deposition of carbon on catalyst surface.

2.4 Reaction study

According to a previously reported procedure\(^2\). The temperature-programmed reaction of ethanol dehydration was done by increasing temperature from 200°C until 400°C. The ethanol dehydration was carried out in a fixed-bed continuous down flow microreactor (I.D. = 0.7 cm) at atmospheric pressure which 0.01 g of a packed quartz wool and about 0.05 g of catalyst was pretreated in argon at 200°C for 1 h. The ethanol was fed into the vaporizer and ethanol flow rate was controlled by a single syringe pump at 1.45 ml/h [WHSV = 22.9 (g\(_\text{ethanol} \cdot \text{cat}^{-1}) \cdot \text{h}^{-1}]\). A Shimadzu (GC-14B) gas chromatograph with flame ionization detector (FID) using capillary column (DB-5) at 150°C was used to detect the effluents. Three parameters including conversion of ethanol (\(X_{\text{EtOH}}\)), product selectivity (\(S_i\)) and product yields (\(Y_i\)) characterized the catalytic activity. They were calculated following Eqs. [1], [2] and [3]:

\[
X_{\text{EtOH}}(\%) = \frac{n_{\text{EtOH}}(\text{in}) - n_{\text{EtOH}}(\text{out})}{n_{\text{EtOH}}(\text{in})} \times 100 \quad [1]
\]

\[
S_i(\%) = \frac{n_i}{\sum n_i} \times 100 \quad [2]
\]

\[
Y_i(\%) = \frac{X_{\text{EtOH}} \times S_i}{100} \quad [3]
\]

3 RESULTS AND DISCUSSION

3.1 Characteristics

After various HCl loadings on MMT catalyst, the HCl-activated MMT catalysts were characterized using various techniques. The results are discussed below.

The XRD patterns of all samples are shown in Fig. 1. It can be seen that the characteristic peaks at \(2\theta = 5.9, 20, 22\) and 36° were assigned to the smectite\(^{20}\). In the MMT after acid treatment, it was informed that the peak at 20 = 21.8° having basal distance of 4.08 Å is the impurities\(^{21}\). The reflection peaks of all HCl acid-activated montmorillonite were still in the same position excepting for 0.05 M-MMT catalyst. The XRD peaks of 0.05 M-MMT catalyst were shifted to lower degrees due to the expansion of the basal spacing\(^{20}\). The intensity of peaks of lower acid concentration activated MMT such as 0.05 M-MMT, 0.1 M-MMT, 0.3 M-MMT, 0.5 M-MMT was similar. In contrary, at higher acid concentration activated MMT such as 1 M-MMT, 2 M-MMT and 4 M-MMT, it was found that the intensity of peaks apparently decreased indicating the low concentration of crystalline plane. It is known that the active acidic site for the reaction is improved due to increasing of crystallinity\(^{21}\). For most catalysts, it revealed that the main crystalline structure did not significantly change with the acid activation, excepting for the 4 M-MMT sample, where the decreasing of XRD peak at 20 = 20° was observed. It may cause from the excess of acid concentration that destroys the structure of catalyst\(^{21}\).

The FTIR spectra of all acid-activated montmorillonite catalysts are shown in Fig. 2. The functional groups of all acid-activated MMT catalysts can be investigated by FTIR in the wavenumber range of 4000-400 cm\(^{-1}\). All acid-activated MMT catalysts represent adsorption bands at 3417 cm\(^{-1}\). This band is assigned to the stretching vibration of OH groups for physisorbed water molecules on surface\(^{27}\). The OH stretching vibration coordinated to Al\(^{3+}\) cations (Al-OH-Al) was found at 3621 cm\(^{-1}\). The adsorption bands at 1182 cm\(^{-1}\) and 1021 cm\(^{-1}\) were the Si-O for stretching vibration (out-of-plane) and the Si-O stretching (in-plane), respectively. The deformation of Al-OH-Al was corresponding to 912 cm\(^{-1}\) and the peak at 618 cm\(^{-1}\) was assigned to the out

Fig. 1 XRD patterns of all acid-activated montmorillonite catalysts.

Fig. 2 FTIR spectra of all acid-activated montmorillonite catalysts.
of plane of Al-O stretching vibration \(^{26}\). The peak at 793 cm\(^{-1}\) is the impurities such as cristobalite\(^{21,26}\), which did not change after increasing the acid concentration to activate MMT from 0.05 M to 2 M, but it changed the structure of 4 M-MMT catalyst with corresponding to the XRD results.

The surface area and pore structure of all acid-activated catalysts were studied by \(\text{N}_2\) physisorption. The specific surface areas for all acid-activated catalysts are summarized in Table 1. It was found that after activation of MMT with hydrochloric acids, it decreased the surface area due to the passivation process as reported by Ajemba and Onukwuli\(^{28}\). It occurred from the deposition of the free silica of the tetrahedral sheet. Figure 3 represents the pore structures of sample presented as the \(\text{N}_2\) adsorption-desorption isotherms. All catalyst samples show the hysteresis loop at high relative pressure (\(P/P_0 > 0.4\)). Therefore, they are mesoporous structure corresponding to Type IV (IUPAC). Mostly, catalyst samples showed the similar hysteresis loop excepting for 4 M-MMT catalyst. It can be observed that for 4 M-MMT catalyst, the hysteresis loop is much broader indicating larger pore volume than other catalyst samples. A plot of pore size distribution between pore volume and pore diameter also confirms the change in pore structures as seen in Fig. 4. It reveals that the pore diameters of sample are ranged between 2 to 50 nm indicating the mesoporous material.

SEM micrograph can be used to observe the acid activation effect which did not change the morphology of MMT catalyst. Elemental distribution in all catalysts can be quantitatively determined by EDX as shown in Table 2. In the previous study\(^{24}\), it showed that after different acid activations of MMT, it was observed the removal of Al cation in structure and Al\(^{3+}\) ion was probably replaced by H\(^{+}\) ion. Therefore, the Si/Al ratio apparently increased\(^{21}\). Based on this study, raw MMT had the Si/Al ratio of 2.3 and it was found that the Si/Al ratio increased after activation with different acid concentrations. It indicated that higher Brønsted acid sites occurred by the replacement of Al\(^{3+}\) in the structure.

**Table 1** Properties of all acid-activated montmorillonite catalysts.

| Samples       | BET Surface Area, \(S_{\text{BET}}\) (m\(^2\)/g) | \(\text{NH}_3\) Desorption (\(\mu\)mol \(\text{NH}_3\)/g cat.) | Total Acidity (\(\mu\)mol \(\text{NH}_3\)/g cat.) | Acid Density (\(\mu\)mol \(\text{NH}_3\)/m\(^2\)) |
|---------------|-----------------------------------------------|--------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| MMT           | 191                                           | 239.9                                           | 194.7                                         | 434.6                                         | 2.27                                          |
| 0.05M-MMT     | 191                                           | 297.9                                           | 230.2                                         | 528.1                                         | 2.65                                          |
| 0.1M-MMT      | 161                                           | 388.2                                           | 144.5                                         | 532.7                                         | 3.30                                          |
| 0.3M-MMT      | 158                                           | 369.5                                           | 176.9                                         | 546.4                                         | 3.45                                          |
| 0.5M-MMT      | 134                                           | 266.1                                           | 134.8                                         | 400.9                                         | 3.00                                          |
| 0.7M-MMT      | 165                                           | 271.8                                           | 143.3                                         | 415.1                                         | 2.51                                          |
| 1M-MMT        | 172                                           | 261.9                                           | 101.4                                         | 363.3                                         | 2.11                                          |
| 2M-MMT        | 135                                           | 233.4                                           | 108.6                                         | 342.0                                         | 2.53                                          |
| 4M-MMT        | 117                                           | 227.0                                           | 139.8                                         | 366.8                                         | 3.02                                          |

**Fig. 3** \(\text{N}_2\) adsorption–desorption isotherms of all acid-activated montmorillonite catalysts.

**Fig. 4** Pore size distribution of all acid-activated montmorillonite catalysts.
Effect of HCl Loading and Ethanol Concentration over HCl-Activated Clay Catalysts for Ethanol Dehydration to Ethylene

J. Oleo Sci. 66, (12) 1355-1364 (2017)

1359

with H\(^+\) from HCl activation\(^{21}\) over the 0.3 M-MMT catalyst. Among other acid-activated MMT catalysts, this catalyst exhibited the highest Si/Al ratio at 7.4 which can be proven by NH\(_3\)-TPD technique.

The amount of ammonia desorbed from the catalyst can be considered as the number of acid sites and the acid strength presented on the catalyst, related to both Lewis and Brønsted acid sites. It was performed by NH\(_3\)-TPD. The TPD profiles (not shown) for all acid-activated catalysts indicated two different types of acid site and catalysts have a broad peak at 100-500°C, due to the presence of weak, medium and strong acid sites. Generally, the desorption peaks at low temperature below 250°C is corresponding to the weak acid sites, whereas those peaks above 400°C is associated with strong acid sites\(^ {23}\). Previous researches have reported on the strength of acidity such as Chen et al.\(^ {5}\) and Xiao et al.\(^ {29}\). They claimed that the weak, and moderate and strong acidity affected the catalytic activity of ethanol dehydration. Dehydration activity of ethylene is better on the catalysts with higher weak acid site, while strong acid site produces the polymerization of ethylene. The integration of desorption area of ammonia according to the Gauss curve fitting method was used to calculated the number of acid site on catalyst and they are summarized in Table 1.

It was found that the acid sites of MMT increased when it was activated with 0.05 M - 0.3 M hydrochloric acid and decreased with higher acid concentrations. The 0.3 M-MMT catalyst exhibited the largest amount of weak acid site and acid density (3 \(\mu\)moleNH\(_3\)/gcat) which leads to increased amounts of Brønsted acid sites as seen from Table 1. This is corresponding the highest Si/Al as confirmed by EDX results and indicated that 0.3 M-MMT has higher H\(^+\) on surface than other catalysts.

### 3.2 Reaction study

#### 3.2.1 Effect of HCl loading in MMT catalyst

In order to study the effect of difficult HCl loadings, dehydration of ethanol was performed over the different loadings of HCl on MMT catalyst in the temperature range of 200 to 400°C. It is well known that the product distribution of dehydration depends on the reaction temperatures as mentioned earlier. The result as shown in Fig. 5 is obvious that the conversion increased with increasing in the reaction temperature. The 0.3 M-MMT exhibited the highest conversion of 95% at 400°C having ethylene selectivity of 98%. As seen from Table 1, which represented the properties of all HCl-activated MMT catalysts, the 0.3 M-MMT contains the largest amount of weak acid site (ca. 369.5 \(\mu\)mole NH\(_3\)/gcat) and acid density (ca. 3.45 \(\mu\)mole NH\(_3\)/m\(^2\)). Meanwhile, the result represents the difference between low and high acid concentration activated MMT. At low acid concentration, it obtained higher acid sites of catalyst than high acid concentration, which is related to the result in ethanol conversion (Fig. 5). In addition, the increase in amounts of weak acid site for the HCl activation can be explained by EDX results as seen in Table 2. It represented the chemical composition obtained by EDX of HCl-activated MMT catalysts. It revealed that the amounts of weak acid site increased with increasing Si/Al ratio due

![Fig. 5 Ethanol conversions of all acid-activated montmorillonite catalysts.](image)

**Table 2** Chemical composition obtained by EDX of all acid-activated montmorillonite catalysts.

| Samples | % weight | O | Na | Mg | Al | Si | Ca | Ti | Fe | Si/Al |
|---------|----------|---|----|----|----|----|----|----|----|------|
| 0.05M-MMT | 41.39 | 0.30 | 1.64 | 15.08 | 37.61 | 0.51 | 1.07 | 2.45 | 2.5 |
| 0.1M-MMT | 44.08 | 0.53 | 2.23 | 13.19 | 37.22 | 0.57 | 0.4 | 1.78 | 2.8 |
| 0.3M-MMT | 42.63 | 0.44 | 1.09 | 6.32 | 46.76 | 0.37 | 0.99 | 1.41 | 7.4 |
| 0.5M-MMT | 39.77 | 0.18 | 1.24 | 8.49 | 46.26 | 0.56 | 1.14 | 2.35 | 5.4 |
| 0.7M-MMT | 43.64 | 1.05 | 3.13 | 15.4 | 33.46 | 1.07 | 1.3 | 0.95 | 2.2 |
| 1M-MMT | 44.68 | 0.50 | 1.47 | 11.94 | 38.46 | 0.27 | 0.28 | 2.39 | 3.2 |
| 2M-MMT | 41.48 | 0.56 | 1.62 | 15.26 | 38.3 | 0.3 | 0.68 | 1.75 | 2.5 |
| 4M-MMT | 43.53 | 0.34 | 1.15 | 13.10 | 37.84 | 0.44 | 0.68 | 2.92 | 2.9 |
to the replacement of $\text{Al}^{3+}$ by $\text{H}^+$ in the MMT surface\textsuperscript{31}. Therefore, the presence of 0.3 M-MMT catalyst with Si/Al ratio of 7.4 was accompanied by the appearance of the NH$_3$-TPD result.

The ethylene and diethyl ether selectivities obtained by different catalysts are plotted as shown in Figs. 6 and 7, respectively. As seen in these figures, the results appear to be in agreement with the role of ethanol dehydration. For the ethanol dehydration, there are two competitive pathways containing the main path involves the formation of ethylene which occurs via intramolecular that is endothermic and another one, inter-molecular dehydration to diethyl ether, is exothermic\textsuperscript{2,5,30}, which is directly corresponding to the equation (I) and (II) as mentioned above. In case of ethylene (Fig. 6), all catalysts exhibited the highest ethylene selectivity at 400°C and the ethylene selectivity apparently increased with increasing reaction temperature. The result showed that the 2 M-MMT and 4 M-MMT exhibited higher ethylene selectivity than others at 200°C. It may be due to blocking of diethyl ether formation at low reaction temperature. For the diethyl ether selectivity in Fig. 7, the diethyl ether selectivity as opposed to the ethylene selectivity. It decreased with increasing reaction temperature. The result indicated that at 200 to 300°C, diethyl ether is a major product for all catalysts. Increased reaction temperature resulted in a significant decrease in diethyl ether selectivity. However, at low reaction temperature, 2 M-MMT and 4 M-MMT catalysts exhibited lower diethyl ether selectivity than other catalysts due to the formation of ethylene. It apparently demonstrated that the ethylene selectivity and diethyl ether selectivity showed a similar trend at low (0.05 M-1 M) and high (2 M - 4 M) acid concentration activated MMT.

A comparison of ethylene yield (product of ethanol conversion and ethylene selectivity) is considered. The ethylene yield for all catalysts is shown in Fig. 8. It increased with increasing reaction temperature up to 400°C. At this temperature, the highest ethylene yield (93%) was obtained from the 0.3 M-MMT catalyst, which indicated the best catalyst under the condition: 0.3 M, 30ml of HCl, and aging for 1 h under basis 1 g of MMT.

3.2.2 Effect of ethanol concentration in feed
It is well known that the production of bioethanol via fermentation synthesis contains large amount of water. Mostly, the concentration of bioethanol is about 10 wt%. In addition, there is some researcher that study the effect of ethanol concentration on catalyst such as Wu et al.\textsuperscript{31}. They investigated the different concentrations of bio-ethanol aqueous solution of 40, 70, 80, 95, 99.7 wt% on SAPO-34. The catalytic testing showed that both of ethanol conversion and ethylene selectivity over SAPO-34 catalyst decreased with increasing amount of water in ethanol feed. The 99.7 wt% of ethanol at temperature reaction of 240°C, about 98% of ethanol conversion and 99% of ethylene selec-
Effect of HCl Loading and Ethanol Concentration over HCl-Activated Clay Catalysts for Ethanol Dehydration to Ethylene

J. Oleo Sci. 66, (12) 1355-1364 (2017)

lectivity were obtained. However, they decreased to 55% and 80%, respectively with decreasing ethanol concentration to 40 wt%. This might be rationalized by the fact that this catalyst show poor water resistance (hydrothermal effect). Therefore, this research is interested in the effect of ethanol feed concentrations including 10, 30, 50, 80 and 99.95 wt% of ethanol. This is due to simplify the condensation process of bioethanol and carry out in flexible processing on conversions and selectivity.

In this section, 0.3 M-MMT catalyst was used due to it acts as the best catalyst among other catalysts as described in section 3.2.1. The catalytic dehydration of ethanol over 0.3 M-MMT catalysts with various ethanol concentrations in feed was also conducted to measure catalytic activity in terms of ethanol conversion at the reaction temperature from 200 to 400°C. The effect of ethanol concentration on the ethanol conversion, ethylene selectivity, diethyl ether selectivity and ethylene yield are shown in Figs. 9 to 12, respectively. Moreover, all of these experiments were found to produce only little amount of acetaldehyde (~0.1-0.6%) at high reaction temperature.

In Fig. 9, it represented the ethanol conversions of 0.3 M-MMT catalyst under various feed concentration. It obvious that water content did not affect on ethanol conversion of this catalyst. It showed closely ethanol conversion for all studied feed concentration. Using lower ethanol concentration also showed the better ethanol conversion than using pure ethanol as reactant feed. The selectivity of ethylene and diethyl ether were shown in Figs. 10 and 11, respectively. At lower reaction temperature (200-300°C),
the selectivity of ethylene increases with decreasing ethanol concentration, while the selectivity of ethyl ether decreased. This may occur from changing of acid site. In previous work of ethanol over γ-Al₂O₃ catalyst, it was found that Lewis acid site shifts to Brønsted acid site more easily on γ-Al₂O₃ due to increased amount of water concentration that leads to decreased alumina basicity and dehydration activities, which is competitive adsorption of water and ethanol on the active sites of the catalyst surface were proposed. Moreover, at low ethanol concentration, it gave high ethylene selectivity because the weak associatively adsorbed ethanol to react with ethoxy groups was low. However, as see in Fig. 11, the selectivity of diethyl ether tended to decrease with increased water. It is feasible that the effect of water could be removed at high temperature. However, ethylene selectivity was obtained more than 98% at higher reaction temperature. This made the better ethylene yield in bioethanol as shown in Fig. 12. This finding also demonstrated that the hydrothermal effect was less pronounced on the 0.3 M-MMT catalyst at high content of water in ethanol feed. It revealed that this catalyst can be utilized in bioethanol dehydration as a green process to obtain the better catalytic activity.

Nevertheless, it is generally accepted that the most important factor affecting the deactivation of active site is due to coking come from high water content in ethanol reactant. Therefore, the carbon deposition on catalyst surface was studied and determined through the thermal gravimetric analyses (TGA). The TG analysis recorded the actual and different weight from 30°C to 1000°C and represented in Fig. 13.

Figure 13 shows the TGA curves of catalysts after they were spent in dehydration reaction with the ethanol concentration of 10 wt% and 99.95 wt%. Initial weight loss up to 200°C is believed to be due to the removal of water from the catalysts, therefore, it had no effect on the coke calculation. For the temperature range of 200°C to 800°C, the weight loss is used for the coke calculation due to this period is de-coking process. From TGA result, it demonstrated that the spent 0.3 M-MMT catalyst under higher content of water showed the weight loss of 5.02%, which was apparently lower than pure ethanol condition (the weight loss of 8.31%). It can be seen that a large amount of water in reactant did not show a remarkable effect on the rising of carbon deposition of the 0.3 M-MMT catalyst. Therefore, it is of interest that the 0.3 M-MMT catalyst may be used in high water content of ethanol or bioethanol dehydration with low amount of carbon deposition on catalyst surface. However, it still remained highly active catalyst and selectivity of ethylene similar to the use of catalyst in pure ethanol dehydration.

Based on our present study, the high ethylene yield of 93% over 0.3 M-MMT catalyst was obtained. In order to compare the result of the catalysts in this work with other works, the comparative results of ethylene selectivity and ethylene yield are added as shown in Table 3. Many works gave high amount of ethylene yield and selectivity. However, clay is cheaper than other materials, which also gives nearly complete yield and selectivity of ethylene (The best condition can reach the ethanol conversion and ethylene selectivity up to 95% and 98% at reaction temperature of 400°C, respectively).

| Catalysts       | Ethylene selectivity (%) | Ethylene yield (%) | Temperature (°C) |
|-----------------|--------------------------|--------------------|-----------------|
| TiO₂/Al₂O₃ (2)  | 99                       | 99                 | 460             |
| Silica-alumina  | N/A                      | 77                 | 300             |
| Zeolites (4)    | N/A                      | 58-100             | 180             |
| ZrO₂ (38)       | 87                       | 87                 | 500             |
| TiO₂ (38)       | 65                       | 65                 | 500             |
| Clay (This work)| 98                       | 93                 | 400             |
4 CONCLUSION

The catalytic performance for ethanol dehydration over hydrochloric acid-activated montmorillonite catalysts prepared by acid activation was investigated. It was found that the best condition for the preparation of HCl-activated MMT is 0.3 M (30 ml aging for 1 h) under basis of 1 g MMT. This is plausible due to the 0.3 M-MMT catalyst exhibits the highest activity in the study of acid concentration activated MMT because of its physical properties (Si/Al = 7.4) and its acid properties, therefore, this catalyst was led to study in the investigation of ethanol feed concentration. Moreover, it was found that the excess acid concentration activated MMT in 4 M-MMT destroyed the structure of catalyst which were shown in XRD and FTIR characterization. The effect of ethanol concentration or water content on 0.3 M-MMT further catalyst was studied via ethanol dehydration and its acid properties, therefore, this catalyst was led to the best condition for the preparation of HCl-activated montmorillonite catalysts prepared by acid activation.

Acknowledgement

The authors thank the Royal Golden Jubilee Ph.D. scholarship and the research grant (IRG 5780014) from the Thailand Research Fund (TRF) and the Grant for International Research Integration: Chula Research Scholar, Ratchadaphiseksomphot Endowment Fund for financial support of this project.

References

1) Zhang, M.; Yu, Y. Dehydration of ethanol to ethylene. Ind. Eng. Chem. Res. 52, 9505-9514 (2013).
2) Chen, G.; Li, S.; Jiao, F.; Yuan, Q. Catalytic dehydration of bioethanol to ethylene over TiO2/γ-Al2O3 catalysts in microchannel reactors. Catal. Today 125, 111-119 (2007).
3) Wannaborworn, M.; Praserthdam, P.; Jongsomjit, B. A comparative study of solvothermally and sol-gel-derived nanocrystalline aluminas for ethanol dehydration. J. Nanomater. 2015, 1-15 (2015).
4) Takahara, I.; Saito, M.; Inaba, M.; Murata, K. Dehydration of ethanol into ethylene over solid acid catalysts. Catal. Lett. 105, 249-252 (2005).
5) Chen, Y.; Wu, Y.; Tao, L.; Dai, B.; Yang, M.; Chen, Z.; Zhu, X. Dehydration reaction of bio-ethanol to ethylene over modified SAPO catalysts. J. Ind. Eng. Chem. 16, 717-722 (2010).
6) Zhang, X.; Wang, R.; Yang, X.; Zhang, F. Comparison of four catalysts in the catalytic dehydration of ethanol to ethylene. Microporous Mesoporous Mater. 116, 210-215 (2008).
7) Eckert, M.; Fleischmann, G.; Jira, R.; Bolt, H.M.; Golka, K. Acetaldehyde. in Ullmann’s Encyclopedia of Industrial Chemistry. 6th ed. Vol. A1, Wiley-VCH, Weinheim, Germany, pp. 31-44 (2002).
8) Nadeem, A.M.; Waterhouse, G.L.N.; Idriess, H. The reactions of ethanol on TiO2 and Au/TiO2 anatase catalysts. Catal. Today 182, 16-24 (2012).
9) Ramesh, K.; Hui, L.; Han, Y.; Borgna, A. Structure and reactivity of phosphorus modified H-ZSM-5 catalysts for ethanol dehydration. Catal. Commun. 10, 567-571 (2009).
10) Varisli, D.; Dogu, T.; Dogu, G., Ethylene and diethyl ether production by dehydration reaction of ethanol over different heteropolyacid catalysts. Chem. Eng. Sci. 62, 5349-5352 (2007).
11) Amolholoda, S.; Kazemeini, M.; Zaherian, A.; Zakerinasab, M.R. Reaction kinetics determination and neural networks modeling of methanol dehydration over nano γ-Al2O3 catalyst. J. Ind. Eng. Chem. 18, 2059-2068 (2012).
12) Luts, T.; Katz, A. Chemisorption and dehydration of ethanol on silica: Effect of temperature on selectivity. Top. Catal. 55, 84-92 (2012).
13) Phung, T.K.; Busca, G. Ethanol dehydration on silica-aluminas: Active sites and ethylene/diethyl ether selectivities. Catal. Commun. 68, 110-115 (2015).
14) Takahashi, R.; Sato, S.; Sodesawa, T.; Arai, K.; Yabuki, M., Effect of diffusion in catalytic dehydration of alcohol over silica–alumina with continuous macropores. J. Catal. 229, 24-29 (2005).
15) Han, Y.; Lu, C.; Xu, D.; Zhang, Y.; Hu, Y.; Huang, H. Molybdenum oxide modified HZSM-5 catalyst: Surface acidity and catalytic performance for the dehydration of aqueous ethanol. Appl. Catal., A: General 396, 8-13 (2011).
16) Bi, J.; Guo, X.; Liu, M.; Wang, X., High effective dehydration of bio-ethanol into ethylene over nanoscale HZSM-5 zeolite catalysts. Catal. Today 149, 143-147 (2010).
17) Pushpaletha, P.; Rugmini, S.; Lalithambika, M. Correlation between surface properties and catalytic activity of clay catalysts. Appl. Clay Sci. 30, 141-153 (2005).
18) Shirini, F.; Vahid Atghia, S.; Managhanani, M. Sulfonic acid-functionalized ordered nanoporous Na+-montmorillonite as an efficient, eco-benign, and water-tolerant nanoreactor for chemoselective oxathioacetalization of aldehydes. Int. Nano Lett. 3, 1-6 (2013).
19) Yadav, M.K.; Chudasama, C.D.; Jasra, R.V. Isomerisation of α-pinene using modified montmorillonite clays. J. Mol. Catal. A: Chem. 216, 51-59 (2004).

J. Oleo Sci. 66, (12) 1355-1364 (2017)
20) Hart, M. P.; Brown, D. R., Surface acidities and catalytic activities of acid-activated clays. *J. Mol. Catal., A: Chem.* **212**, 315-321 (2004).

21) Leandro, Z.; Luiz, P., Ramos; Fernando, W. Acid activated montmorillonite as catalysts in methyl esterification reactions of lauric acid. *J. Oleo Sci.* **61**, 497-504 (2012).

22) Ravichandran, J.; Lakshmanan, C.M.; Sivasankar, B. Acid activates montmorillonite and vermiculite clays as dehydration and cracking catalysts. *React. Kinet. Catal. Lett.* **59**, 301-308 (1996).

23) Bokade, V.V.; Yadav, G.D. Heteropolyacid supported on montmorillonite catalyst for dehydration of dilute bioethanol. *Appl. Clay Sci.* **53**, 263-271 (2011).

24) Krutpijit, C.; Jongsomjit, B. Catalytic ethanol dehydration over different acid-activated montmorillonite clays. *J. Oleo Sci.* **65**, 347-355 (2016).

25) Rezende, M.J.C.; Pereira, M.S.C.; Santos, G.F.N.; Aroei-ra, G.O.P.; Albuquerque Jr., T.C.; Suarez, P.A.Z.; Pinto, A.C. Preparation, characterization and evaluation of Brazilian clay-based catalysts for use in esterification reactions. *J. Braz. Chem. Soc.* **23**, 1209-1215 (2012).

26) Faghihian, H.; Mohammadi, M.H. Surface properties of pillared acid-activated bentonite as catalyst for selective production of linear alkylbenzene. *Appl. Surf. Sci.* **264**, 492-499 (2013).

27) Bendou, S.; Amrani, M. Effect of hydrochloric acid on the structure of sodic-bentonite clay. *J. Miner. Mater. Charact. Eng.* **2**, 404-413 (2014).

28) Ajemba, R.O.; Onukwuli, O.D., Adsorptive removal of colour pigment from palm oil using acid activated nteje clay. Kinetics, equilibrium and thermodynamics. *Physicochem. Probl. Miner. Process.* **49**, 369-381 (2013).

29) Xiao, Y.; Li, X.; Yuan, Z.; Li, J.; Chen, Y., Catalytic dehydration of ethanol to ethylene on TiO2/4A zeolite composite catalysts. *Catal. Lett.* **130**, 308-311 (2009).

30) Sheng, Q.; Ling, K.; Li, Z.; Zhao, L. Effect of steam treatment on catalytic performance of HZSM-5 catalyst for ethanol dehydration to ethylene. *Fuel Process. Technol.* **110**, 73-78 (2013).

31) Wu, L.; Zhou, T.; Cui, Q.; Wang, H.; Hu, Y.; Huang, H. The catalytic dehydration of bio-ethanol to ethylene on SAPO-34 catalysts. *Pet. Sci. Technol.* **31**, 2414-2421 (2013).

32) Golay, S.; Doepper, R.; Renken, A. Reactor performance enhancement under periodic operation for the ethanol dehydration over c-alumina, a reaction with a stop-elect. *Chem. Eng. Sci.* **54**, 4469-4474 (1999).

33) Phung, T.K.; Lagazzo, A.; Rivero Crespo, M.A.; Sánchez Escribano, V.; Busca, G. A study of commercial transition aluminas and of their catalytic activity in the dehydration of ethanol. *J. Catal.* **311**, 102-113 (2014).

34) Aguayo, A.T.; Gayubo, A.G.; Atutxa, A.; Olazar, M.; Bilbao, J. Catalyst deactivation by coke in the transformation of aqueous ethanol into hydrocarbons. Kinetic modeling and acidity deterioration of the catalyst. *Ind. Eng. Chem. Res.* **41**, 4216-4224 (2002).

35) Aguayo, A.T.; Gayubo, A.G.; Tarrio, A.M.; Atutxa, A.; Bilbao. J. Study of operating variables in the transformation of aqueous ethanol into hydrocarbons on an HZSM-5 zeolite. *J. Chem. Technol. Biotechnol.* **77**, 211-216 (2002).

36) Oudejans, J.C.; Van Den Oosterkamp, P.F.; Van Bekkum, H. Conversion of ethanol over zeolite h-zsm-5 in the presence of water. *Appl. Catal.* **3**, 109-115 (1982).

37) Ahmed, R.; Sinnathambi, C.M.; Subbarao, D. Kinetics of de-coking of spent reforming catalyst. *Journal of Applied Sciences* **11**, 1225-1230 (2011).

38) Phung, T.K.; Proietti Hernandez, L.; Busca, G. Conversion of ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia. *Appl. Catal., A: General* **489**, 180-187 (2015).