Catalytic Ethanol Dehydration over Different Acid-activated Montmorillonite Clays

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Abstract: In the present study, the catalytic dehydration of ethanol to obtain ethylene over montmorillonite clays (MMT) with mineral acid activation including H_2SO_4 (SA-MMT), HCl (HA-MMT) and HNO_3 (NA-MMT) was investigated at temperature range of 200 to 400°C. It revealed that HA-MMT exhibited the highest catalytic activity. Ethanol conversion and ethylene selectivity were found to increase with increased reaction temperature. At 400°C, the HA-MMT yielded 82% of ethanol conversion having 78% of ethylene yield. At lower temperature (i.e. 200 to 300°C), diethyl ether (DEE) was a major product. The highest activity obtained from HA-MMT can be attributed to an increase of weak acid sites and acid density by the activation of MMT with HCl . It can be also proven by various characterization techniques that in most case, the main structure of MMT did not alter by acid activation (excepted for NA-MMT). Upon the stability test for 72 h during the reaction, the MMT and HA-MMT showed only slight deactivation due to carbon deposition. Hence, the acid activation of MMT by HCl is promising to enhance the catalytic dehydration of ethanol.

Key words: ethanol, catalytic dehydration, montmorillonite clay, acid activation

1 INTRODUCTION

Ethylene, one of the most important chemicals in the petrochemical industry, is used as feedstock to produce polyethylene, ethylene oxide, ethyl benzene, ethylene glycol, styrene monomer and etc. At present, ethylene is produced via thermal cracking reaction of petroleum or natural gas feedstock, which consumes high energy because it is highly endothermic reaction. Hence, the alternative way to convert ethanol into ethylene via catalytic dehydration is captivating since ethanol is derived from renewable feedstocks. In order to achieve the catalytic dehydration, solid acid catalysts such as alumina, silica-alumina, zeolite, titania-silica, are necessary. These solid acid catalysts have been widely studied for the catalytic ethanol dehydration¹⁾. More recent reviews on the solid acid catalysts, which have been studied for the catalytic ethanol dehydration, were also composed of HZSM-5²⁾, SAPO^{3, 4)}, heteropolyacids⁵⁻⁸⁾, and zirconia-titania⁹⁾. Sheng *et al.*²⁾ reported that the steam treatment of HZSM-5 catalyst was the key to obtain high ethanol conversion and ethylene selectivity. The SAPO catalysts were studied by Arias *et al.*³⁾ and Zhang *et al.*⁴⁾. They found that the modification of SAPO with nickel apparently increased ca. 2% of ethylene yield.

The heteropolyacids (HPAs) were studied by several researchers⁵⁻⁸⁾. Phung *et al.*⁹⁾ also studied the use of zirconia and titania catalysts. They found that high conversion of ethanol and ethylene selectivity can be obtained using tungsten to modify zirconia and titania. However, the coke formation can occur leading to low stability of these catalysts.

Among other solid acid catalysts, clays have been potentially used in some organic synthesis such as alkylation of phenols¹⁰⁾ and dimerization and/or polymerization of unsaturated hydrocarbons¹¹⁾ because they have high surface area, sorptive, cheapness, easy modification, non-corrosive and recyclability^{12, 13)}. In fact, montmorillonite (MMT), containing acidic cations, metal complexes, and photocatalytically active cations, is the smectite group minerals of clay used in the catalytic application. This group has a dioctahedral or trioctahedral 2:1 layer structure. It is high cation-exchange capacity (CEC) and good swelling properties. Moreover, MMT also used as Brønsted acid catalyst, which can improve acid site and increase surface area by acid treatment under harsh conditions¹⁴⁾. Acid-activated MMT clays are widely used in many industries, for instance, foodstuff, mineral oil, beverage and sugar, chemical and

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paper industry¹⁵. They are also employed as catalysts and catalyst supports in several reactions such as isomerization¹⁶, alkylation¹⁷, acrylation¹⁸ and dehydration¹⁹. Treatment of clay with acid can exchange cations with hydrogen ions and leach aluminium from the central octahedral lattice layer of the clay¹⁹.

Based on the previous works in catalytic dehydration of ethanol^{20–23}, the use of phosphoric acid gave the high ethylene yield, but it generated coke formation resulting in rapid deactivation. When heteropolyacid (HPA) having the Keggin structure was employed as a catalyst for dehydration of dilutes bioethanol, it decreased the selectivity of ethylene. In addition, the MMT-supported HPA catalyst is good for dehydration reaction because it increases the selectivity of ethylene. However, due to its high preparation cost, the application of this catalyst is limited. Therefore, the use of cheaper mineral acids such as sulfuric acid, hydrochloric acid and nitric acid is essentially captivating for activation of MMT.

For the best of our knowledge, the catalytic dehydration of gas-phase ethanol over the MMT or acid-activated MMT has not been yet investigated. Hence, the main objective of this study is to develop a better understanding on changes in characteristics and catalytic properties of MMT with acid activation via the catalytic dehydration of ethanol. Three kinds of acid including sulfuric acid, hydrochloric acid and nitric acid were employed for the purpose.

2 EXPERIMENTAL

2.1 Materials

The commercial Al-pillared MMT clay (obtained from Aldrich Chemical Company) was employed. Other chemicals used to activate the MMT clay were 95–97% sulphuric acid, 37% hydrochloric acid and 70% nitric acid (obtained from Sigma-Aldrich Chemical Company, Inc.).

2.2 Preparation of acid-activated MMT

The acid activation was done by stirring 1 g of MMT in desired acid solution (0.5 M, 30 ml of sulfuric acid, hydrochloric acid and nitric acid) for 1 h. Then, acid-activated MMT were kept in an oven at 125°C for 21 h. All samples were washed with distilled water until neutral, and then samples were dried at 110°C overnight. The acid-activated MMT catalysts were denoted as SA-MMT, HA-MMT and NA-MMT for the MMT activation with sulfuric acid, hydrochloric acid and nitric acid, respectively.

2.3 Characterization

Characterization of catalysts was performed by several techniques as follows; *Powder X-ray diffraction (XRD)*: XRD patterns of all catalyst samples were determined by X-ray diffractometer (Bruker AXS Model D8 Discover). The

experiment was done by using CuK α radiation source ($\lambda = 1.54439$ Å) with Ni filter in the 2 θ range of 3 to 45° with a resolution of 0.02°.

N₂ physisorption: The specific surface area, pore volume and pore size diameter were determined by nitrogen physisorption. The gas adsorption and desorption isotherms were collected at liquid nitrogen temperature (–196°C) using Micromeritics Chemisorb 2750 Pulse chemisorption system instrument.

Fourier transform infrared spectroscopy (FTIR): The IR spectra were recorded using Nicolet 6700 FTIR spectrometer in the range of 400 to 4000 cm^{–1} to identify specific structural characteristics of the chemical group from the vibration properties.

Temperature-programmed desorption of ammonia (NH₃-TPD): NH₃-TPD was performed using Micromeritics chemisorp 2750 pulse chemisorption system to study the acid properties. In the study, 0.05 g of catalyst was packed in a U-tube glass with 0.03 g of quartz wool and pretreated at 500°C under helium flow for 1 h. Then, the sample was saturated with 15% of NH₃/He and the physisorbed ammonia was desorbed under helium gas flow after saturation. The sample was heated from 40°C to 500°C at heating rate of 10°C/min.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX): SEM and EDX were used to investigate the morphology and elemental distribution of catalysts, respectively using Hitachi mode S-3400N. Micrographs were taken at the accelerating voltage of 30 kV and magnification ranging from 1,000 to 10,000 and the resolution of 3 nm. The SEM was operated using the secondary scattering electron (SE) mode. EDX was performed using Apollo X Silicon Drift Detector Series by EDAX. Before the SEM observation, the sample was conductive to prevent charging by coating with platinum particle under the ion sputtering device.

Thermal gravimetric analysis (TGA): TGA was used to determine the coke deposition on spent catalysts. The sample was analyzed under nitrogen atmosphere at the flow rate of 100 ml/min and heated from room temperature to 1000°C with a heating rate of 10°C/min by thermal gravimetric SDT analyzer model Q600.

2.4 Catalytic ethanol dehydration reaction

2.4.1 Temperature-programmed reaction

In the experiment, 0.01 g of a packed quartz wool and 0.05 g of catalyst were loaded into the fixed-bed continuous flow microreactor with an inside diameter of 0.7 cm, and then the catalyst was pretreated in argon (60 ml/min) at 200°C for 1 h to remove any moisture on surface of catalyst. The liquid ethanol was vaporized in a flowing of argon by controlled injection with a single syringe pump at a constant flow rate of ethanol 1.45 ml/h [WHSV = 22.9 (g_{ethanol}/g_{cat} h^{–1})]. The ethanol dehydration reaction temperature was in-

Scheme 1 Catalytic reaction system of ethanol dehydration.

creased from 200°C to 400°C. Effluents were measured by a Shimadzu (GC-14B) gas chromatograph with flame ionization detector (FID) using capillary column (DB-5) at 150°C. The ethanol dehydration system is displayed in **Scheme 1**. Upon the reaction test, at least three times for each value were recorded. The average value as a function of temperature was reported.

2.4.2 Stability test

The experimental apparatus and set-up were similar with temperature-programmed reaction as mentioned above. The ethanol dehydration temperatures are in range of 340°C (HA-MMT), 400°C (MMT), 430°C (NA-MMT) and 515°C (SA-MMT) depending on the activity of catalysts. After pretreatment catalyst for 1 h, the ethanol with WHSV $22.9 (\text{g}_{\text{ethanol}}/\text{g}_{\text{cat}}^{-1})\text{h}^{-1}$ was fed into the reactor for 10 minutes before sampling the first product. Then, the effluent was collected every 4 h for 48 h and continued every 2 h for 72 h. Effluents were analyzed with the same method as mentioned in 2.4.1.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The MMT and acid-activated MMT such as SA-MMT, HA-MMT and NA-MMT catalysts were characterized using several techniques as mentioned before. The crystalline structure of the MMT and acid-activated MMT catalysts can be identified by XRD measurement. The XRD patterns of all catalysts are shown in **Fig. 1**. As seen, MMT exhibited the XRD characteristic peaks around $2\theta = 5.9^\circ$ indicating the smectite²⁴⁾ and $2\theta = 20, 22$ and 36° . It was reported that the peak at $2\theta = 21.8^\circ$ having basal distance of 4.08 Å is the impurities such as cristobalite and tridimite remain-

Fig. 1 XRD patterns of catalysts.

ing in the MMT after acid treatment²⁵⁾. The basal spacing (d_{001}) reflection of MMT is 15.2 Å at 2θ of 5.8, SA-MMT is 15.0 Å at 2θ of 5.9, HA-MMT is 14.8 Å at 2θ of 5.9 and NA-MMT is 14.8 Å at 2θ of 5.9. The reflection peaks shift to lower degrees, therefore it can be indexed expansion of the basal spacing²⁶⁾. The intensity peak of HA-MMT apparently increased significantly indicating the high concentration of crystalline plane. It is known that when crystallinity increases, it improves the active acidic site for the reaction²⁰⁾. For all catalysts, it revealed that the main crystalline structure did not significantly change with the acid activation, excepting for the NA-MMT sample, where the disappearance of XRD peak at $2\theta = 20^\circ$ was observed.

The functional groups in all catalysts can be identified by FTIR. The FTIR spectra of the MMT and acid-activated MMT catalysts are shown in **Fig. 2**. The MMT presents ad-

Fig. 2 FTIR spectra of catalysts.

sorption bands at 3417 cm^{-1} assigned to the stretching vibration of OH groups for physisorbed water molecules on clay surface²⁷, 3621 cm^{-1} from OH stretching vibration coordinated to Al^{3+} cations (Al-OH-Al)²⁷, 1182 cm^{-1} and 1021 cm^{-1} from Si-O stretching vibration (out-of-plane) and Si-O stretching (in-plane), 912 cm^{-1} from deformation of Al-OH-Al, and 618 cm^{-1} from Al-O stretching vibration (out of plane)²⁶. The peak at 793 cm^{-1} is the cristobalite impurities^{25, 26}, which did not change after acid activation corresponding to the XRD results.

The surface area and pore structure of all catalysts were determined by N_2 physisorption. The specific surface areas for all catalysts are summarized in Table 1. It revealed that after activation of MMT with three mineral acids, it decreased the surface area. This is due to the deposition of the free silica of the tetrahedral sheet by process passivation as reported by Ajemba and Onukwuli²⁸. The pore structures of sample presented as the N_2 adsorption-desorption isotherms are shown in Fig. 3. All samples display the hysteresis loop at high relative pressure ($P/P_0 > 0.4$) indicating that they are mesoporous structure corresponding to Type IV (IUPAC). However, it can be observed that with nitric acid activation of MMT (NA-MMT), the hysteresis loop is much broader indicating larger pore volume than

Fig. 3 N_2 adsorption-desorption isotherms of catalysts.

Fig. 4 Pore size distribution of catalysts.

SA-MMT and HA-MMT samples. This is probably due to some modification on pore structure of MMT, which is related to the disappearance of XRD peak at $2\theta = 20^\circ$ for NA-MMT sample. The change in pore structures is confirmed by a plot of pore volume and pore diameter as seen in Fig. 4. It can be also observed that the pore diameters of sample are ranged between 2 to 50 nm indicating the mesoporous material.

Table 1 Properties of catalyst samples.

Samples	BET Surface Area, S_{BET} (m^2/g)	NH ₃ Desorption ($\mu\text{mol NH}_3/\text{g cat.}$)		Total Acidity ($\mu\text{mol NH}_3/\text{g cat.}$)	Acid Density ($\mu\text{mol NH}_3/\text{m}^2$)
		Weak	Medium to strong		
MMT	191.2	239.9	194.7	434.6	2.27
SA-MMT	101.9	62.1	28.9	91.0	0.89
HA-MMT	133.5	266.1	134.8	400.9	3.00
NA-MMT	171.0	231.6	154.2	385.8	2.25

Table 2 Chemical composition obtained by EDX of all catalysts.

Samples	% weight								
	Na	Mg	Ca	Ti	Fe	O	Al	Si	Si/Al
MMT	0.83	1.67	0.77	1.84	3.37	39.38	14.34	37.80	2.64
SA-MMT	0.20	2.50	0.66	1.02	3.33	41.56	10.78	39.95	3.71
HA-MMT	0.18	1.24	0.56	1.14	2.35	39.77	8.49	46.26	5.45
NA-MMT	0.92	0.91	0.42	0.59	2.03	40.28	10.99	43.85	3.99

Scheme 2 A conceptual model for increased Brønsted acid sites by acid activation.

It can be observed by SEM that the acid activation did not change the morphology of MMT catalyst (not shown). Elemental distribution in all catalysts can be quantitatively determined by EDX as shown in **Table 2**. The main components of samples are O, Si, and Al, whereas other elements are present as impurities. After activation of MMT, the Si/Al ratio apparently increased because of the removal of Al cation in structure and Al^{3+} ion was probably replaced by H^+ ion as illustrated in **Scheme 2**. Among other acid-activated MMT catalysts, HA-MMT exhibited the highest Si/Al ratio (5.45) revealing that higher Brønsted acid sites occurred by the replacement of Al^{3+} with H^+ from HCl activation²⁵⁾. The increase in acidity can be proven by NH_3 -TPD measurement.

The surface acidity and strength of acid site for catalysts are the key factor to determine the catalytic dehydration activity of ethanol. Hence, NH_3 -TPD was performed. The TPD profiles (not shown) for all catalysts indicated two different types of acid site. The desorption peak at low temperature below 250°C was defined as weak acid site and higher temperature around 400°C was described as strong acid site. The number of acid site on catalyst can be calculated by integration of desorption area of ammonia according to the Gauss curve fitting method and summarized in **Table 1**. The result shows that all catalysts had higher weak acid site than moderate to strong acid site and HA-MMT exhibited the largest amount of weak acid site. This can be attributed to H^+ ions for HCl activation can replace more Al^{3+} , which is corresponding the highest Si/Al (5.45) as confirmed by EDX results. This leads to increased

amounts of Brønsted acid sites. The acid density of HA-MMT also increased (from 2.27 to $3 \mu\text{mole NH}_3/\text{m}^2$) as seen from **Table 1**. This indicated that HA-MMT had more H^+ ions on surface than other catalysts. Chen *et al.*²⁹⁾ and Xiao *et al.*³⁰⁾ reported that the weak, and moderate and strong acidity affected the catalytic activity of ethanol dehydration. Catalysts with higher weak acid site show better dehydration activity of ethylene, while polymerization to ethylene is produced by strong acid site.

3.2 Catalytic dehydration of ethanol

The catalytic dehydration of ethanol over MMT and different acid-activated MMT catalysts was conducted to measure catalytic activity in terms of ethanol conversion at the reaction temperature from 200 to 400°C . It is well known that the ethanol conversion increases with increasing reaction temperature. The ethylene selectivity also increases with increasing temperature since this reaction is endothermic as shown in reaction (1). However, at low temperature, the major product is diethyl ether (DEE) as shown in reaction (2) since it undergoes via exothermic reaction.

Based on this study, the results of ethanol conversion upon different reaction temperature are shown in **Fig. 5**. As expected, all catalysts exhibited the similar behavior, where the ethanol conversion increased with increasing

Fig. 5 Ethanol conversions of catalysts.

the reaction temperature from 200 to 400°C. The highest conversion of ethanol was obtained at 400°C for all catalysts. It was found that HA-MMT exhibited the highest ethanol conversion (82%) among other catalysts. It can be observed that at this temperature, the conversion of ethanol decreased in the order of HA-MMT > MMT > NA-MMT > SA-MMT catalysts. This is clearly attributed to both amounts of weak acid site and acid density in the catalysts. As seen from Table 1, the HA-MMT contains the largest amount of weak acid site (ca. 266 $\mu\text{mole NH}_3/\text{g}_{\text{cat}}$) and acid density (ca. 3 $\mu\text{mole NH}_3/\text{m}^2$), while the lowest amount of weak acid site (ca. 62 $\mu\text{mole NH}_3/\text{g}_{\text{cat}}$) and acid density (ca. 0.9 $\mu\text{mole NH}_3/\text{m}^2$) was evident for SA-MMT. In addition, the increase in amounts of weak acid site for the HCl activation can be explained by the increased Si/Al ratio (Table 2) due to the replacement of Al^{3+} by H^+ in the MMT.

The ethylene selectivity obtained at different temperatures is plotted as shown in Fig. 6. It apparently increased with increasing the temperature. All catalysts exhibited the highest ethylene selectivity at 400°C. Fig. 7 shows the DEE selectivity. It indicated that at 200 to 300°C, DEE is a major product for all catalysts. Increased reaction temperature resulted in a significant decrease in DEE selectivity. Although this study focuses on catalytic dehydration of ethanol to obtain ethylene as a major product, 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. Essentially, it increased with increasing reaction temperature up to 400°C. At this temperature, the highest ethylene yield (78%) was obtained from the HA-MMT catalyst.

In order to determine the carbon deposition on the spent catalysts, TGA was also performed. The TGA profiles for all catalysts are shown in Fig. 9. It was found that all catalysts exhibited the similar trend of the TGA patterns. The weight loss (%) related to the amounts of carbon deposition

Fig. 6 Ethylene selectivity of catalysts.

Fig. 7 DEE selectivity of catalysts.

Fig. 8 Ethylene yield of catalysts.

was in the order of HA-MMT (5.3%) > MMT (5.0%) > NA-MMT (4.3%) > SA-MMT (3.9%). It should be noted

Fig. 9 Thermal gravimetric analysis (TGA) of catalysts.

Fig. 10 Stability test for all catalysts at ca. 80% conversion of ethanol.

that the amounts of carbon deposition for each catalyst are insignificantly different. The stability test with time on stream (TOS) of 72 h was performed for all catalysts. The reaction temperature was varied for each catalyst [i.e. 340°C (HA-MMT), 400°C (MMT), 430°C (NA-MMT) and 515°C (SA-MMT)] in order to fix the ethanol conversion at ca. 80%³¹⁾. The results are shown in Fig. 10. For SA-MMT, the ethanol conversion dramatically decreased when compared with other catalysts due to high temperature operation leading to degradation of catalyst and high amount of carbon deposition. The NA-MMT catalyst exhibited more decreased ethanol conversion than that of MMT and HA-MMT because of higher reaction temperature and larger amounts of strong acid site that cause coke formation from further ethylene polymerization. In addition, the result shows only slight difference in stability between MMT and HA-MMT. Thus, the HCl activation of MMT not only enhanced the catalytic dehydration of ethanol, but

also maintained high stability during the reaction as well.

Due to high energy consumption and high cost of steam cracking to produce ethylene, the catalytic dehydration of ethanol to ethylene using the acid-modified clays was investigated as an alternative method. This catalytic dehydration method can occur at lower temperature (ca. 400°C) achieving high conversion of ethanol and selectivity to ethylene. Besides, this process uses ethanol as a renewable raw material. Moreover, both ethanol and clays are cheap and available in Thailand. Therefore, this study will provide beneficial information to further develop the catalytic dehydration of ethanol in the near future.

4 CONCLUSION

The study revealed that among three kinds (H_2SO_4 , HCl and HNO_3) of acid activation of MMT, the HA-MMT (HCl activation) exhibited the highest activity with 82% conversion of ethanol and 78% yield of ethylene at 400°C. The activation of HCl apparently resulted in increased weak acid sites and acid density. The increase in amount of weak acid sites is related to an increase in Brønsted acid sites leading to enhance catalytic activity of ethanol dehydration. The high selectivity of DEE was obtained at lower temperature with also lower conversion of ethanol. This is challenging to increase the DEE yield at such a low temperature. Thus, a chemical promoter is perhaps necessary. The HA-MMT showed only slight deactivation after 72 h used with less carbon deposition.

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