

Research Article

Effect of Calcination Temperatures and Mo Modification on Nanocrystalline (γ - χ)- Al_2O_3 Catalysts for Catalytic Ethanol Dehydration

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The mixed gamma and chi crystalline phase alumina (M-Al) catalysts prepared by the solvothermal method were investigated for catalytic ethanol dehydration. The effects of calcination temperatures and Mo modification were elucidated. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, transmission electron microscopy (TEM), and NH_3 -temperature programmed desorption (NH_3 -TPD). The catalytic activity was tested for ethylene production by dehydration reaction of ethanol in gas phase at atmospheric pressure and temperature between 200°C and 400°C. It was found that the calcination temperatures and Mo modification have effects on acidity of the catalysts. The increase in calcination temperature resulted in decreased acidity, while the Mo modification on the mixed phase alumina catalyst yielded increased acidity, especially in medium to strong acids. In this study, the catalytic activity of ethanol dehydration to ethylene apparently depends on the medium to strong acid. The mixed phase alumina catalyst calcined at 600°C (M-Al-600) exhibits the complete ethanol conversion having ethylene yield of 98.8% (at 350°C) and the Mo-modified catalysts promoted dehydrogenation reaction to acetaldehyde. This can be attributed to the enhancement of medium to strong acid with metal sites of catalyst.

1. Introduction

Ethylene is intermediate in the petroleum industry and used as feedstocks to produce a variety of polymers in petrochemical industry such as polyethylene, polyvinyl chloride, and polystyrene. Therefore, the demand of ethylene continually increases. The total consumption of ethylene and other light olefins was around 174 millions of tons in 2004. It continuously increased up to 205 million tons in 2010 and it is predicted to grow up to 259 million tons in 2016 [1]. Moreover, ethylene is used as the precursor for synthesis of ethylene oxide, ethylene dichloride, ethylbenzene, and so on [2–5]. Traditionally, ethylene is obtained from the thermal catalytic cracking of petroleum and natural gas upon an endothermic reaction requiring high temperatures (600°C–1000°C) [2]. Since petroleum is nonrenewable resource, the new suitable way to produce ethylene from renewable resource is considered [6]. Hence, the dehydration of ethanol

has been considered as a promising alternative approach to produce ethylene instead of using petroleum as feedstock.

Dehydration of ethanol over solid acid catalysts requires lower temperature compared to the thermal cracking, leading to the reduction of energy cost. Therefore, many researchers have developed the ethanol dehydration for producing ethylene using solid catalysts. The main product from this reaction is ethylene, whereas diethyl ether, acetaldehyde, and light olefins are byproducts. The acid nature of solid catalyst has direct influence on the dehydration activity. The common solid catalysts such as zeolites [2, 7, 8] and alumina (Al_2O_3) [3, 9] have been applied to study the effect of acidity of catalyst on the dehydration ability. Lu et al. (2011) [7] found that HZSM-5 zeolite catalyst exhibits the highest selectivity of ethylene when it was carried out at low temperature (200°C–300°C). However, HZSM-5 zeolites have too high acidity, which can be rapidly deactivated by coke formation. The formation of coke on the catalyst causes lower stability. Previous works

have been reported that acidity not only strongly affected the dehydration ability but also influenced the reaction stability of catalyst. For γ - Al_2O_3 catalyst, the dehydration reaction must be applied at higher temperature (400–450°C) to achieve high activity. Therefore, many attempts have been tried to modify γ - Al_2O_3 by adding metal oxide on solid support such as iron oxide and titanium oxide [10, 11]. Chen et al. (2007) [11] found that the modification of γ - Al_2O_3 with TiO_2 can improve acidity. The conversion of ethanol is reached to 99.96%, whereas ethylene selectivity is about 99.4% at 440°C. Although the modified γ - Al_2O_3 catalyst required higher temperature than HZSM-5 zeolite catalyst, it is easy to synthesize and the stability of modified γ - Al_2O_3 catalyst is better.

γ - Al_2O_3 catalyst is interesting because of its excellent thermal stability, fine particle size, high surface area, and side reaction inhibition. Khom-in et al. (2008) [12] studied the synthesis of mixed γ - and χ -phase Al_2O_3 catalysts and applied for methanol dehydration. They reported that the acidity of mixed γ - and χ -phase Al_2O_3 is higher than γ - Al_2O_3 and χ - Al_2O_3 [13, 14]. The mixed γ - and χ -phase Al_2O_3 catalysts can be directly synthesized via solvothermal method by using the suitable solvent in order to control structures, grain sizes, and morphologies by varying process conditions. In this research, we focused on the development of the alumina-based solid acid catalysts for ethanol dehydration. The catalysts were synthesized, characterized, and tested at a specified reaction condition. The synthesis parameters, such as calcination temperature and Mo modification influencing dehydration reaction, were varied in order to explore the suitable catalysts for ethanol dehydration.

2. Experimental

2.1. Preparation of Mixed Phase Alumina Catalyst. The mixed γ - and χ -crystalline phase alumina (M-Al) were prepared by the solvothermal method as reported by Janlamool and Jongsomjit [15]. The obtained powders were calcined in a tube furnace at different temperatures including 400°C (M-Al-400), 600°C (M-Al-600), 800°C (M-Al-800), and 1000°C (M-Al-1000) with a heating rate of 10°C/min in air for 6 h.

2.2. Preparation of Mo-Modified M-Al Catalysts. The Mo-modified M-Al catalysts were prepared by impregnation of the mixed phase alumina with an aqueous solution of ammonium heptamolybdate-tetrahydrate $[(\text{NH}_4)_5\text{Mo}_7\text{O}_{34}\cdot 4\text{H}_2\text{O}]$ with various loadings of Mo (5, 10, 15, and 20 wt%). The procedure for preparation catalyst as mentioned above was calculated based on 1 g of catalyst used. First, ammonium heptamolybdate-tetrahydrate was dissolved in 0.6 mL of deionized water. Then, the solution was added dropwise into approximately 1 g of dried solid catalyst. The obtained catalyst was dried in air at room temperature for 24 h, dried in oven at 110°C for 6 h, and calcined in air at 500°C for 2 h.

2.3. Catalyst Characterization

2.3.1. X-Ray Diffraction (XRD). The X-ray diffraction (XRD) patterns relating to bulk crystal structure of the catalysts were

determined by the SIEMENS D5000 X-ray diffractometer. The experiment was carried out using Cu K_α radiation source ($\lambda = 1.54439 \text{ \AA}$) with Ni filter in the 2θ range of 20 to 80° with a resolution of 0.02°.

2.3.2. Nitrogen Physisorption. The BET surface area, pore volume, and pore diameter of catalysts were determined by nitrogen gas adsorption at liquid nitrogen temperature (−196°C) using Micromeritics ChemiSorb 2750 Pulse chemisorption system instrument.

2.3.3. Transmission Electron Microscopy (TEM). The morphology and crystallite size of all catalysts were observed by using JEOL-JEM 200CX transmission electron microscope operated at 100 kV.

2.3.4. Temperature Programmed Adsorption (NH_3 -TPD). The acid properties of catalysts were investigated by temperature-programmed desorption of ammonia (NH_3 -TPD) equipment using Micromeritics ChemiSorb 2750 Pulse Chemisorption System. 0.1 g of catalyst was loaded in a quartz tube and pretreated at 500°C under helium flow. The sample was saturated with 15% NH_3/He . After saturation, the physisorbed ammonia was desorbed under helium gas flow about 30 min, and then it was heated from 40°C to 800°C at heating rate of 10°C/min.

2.4. Reaction Test. The dehydration of ethanol was carried out in a fixed-bed continuous flow reactor with an inner diameter of 7 mm. In the experiment, 0.05 g of catalyst was loaded into the reactor and pretreated in argon (50 mL/min) at 200°C for 1 h under atmospheric pressure. To start the reaction, ethanol was delivered by bubbling argon as a carrier gas through the saturator at 45°C to control the vapor pressure of ethanol with WHSV of 8.4 ($\text{g}_{\text{ethanol}}\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$). The reaction was carried out in temperature ranging from 200°C to 400°C. The products were analyzed by a Shimadzu GC8A gas chromatograph with FID using capillary column (DB-5) at 150°C.

3. Results and Discussion

3.1. Effect of Calcination Temperature

3.1.1. Characteristics. The mixed phase alumina catalysts, calcined at different temperatures, were confirmed by XRD results (Figure 1). It was found that the XRD patterns of M-Al-400, M-Al-500, M-Al-600, M-Al-700, M-Al-800, and M-Al-900 (calcined at 400°C to 900°C) were similar. These patterns indicated the presence of γ -crystalline (32°, 37°, 39°, 45°, 61°, and 66°) and χ -crystalline (37°, 40°, 43°, 46°, 60°, and 67°) phases of alumina [12]. However, the M-Al-1000 catalyst (calcined at 1000°C) exhibits the different XRD pattern due to phase transformation to delta and theta phases [16].

BET surface area, pore volume, and pore size diameter of catalysts with various calcination temperatures are summarized in Table 1. The BET surface area slightly decreased with increasing calcination temperature. Surface area decreased

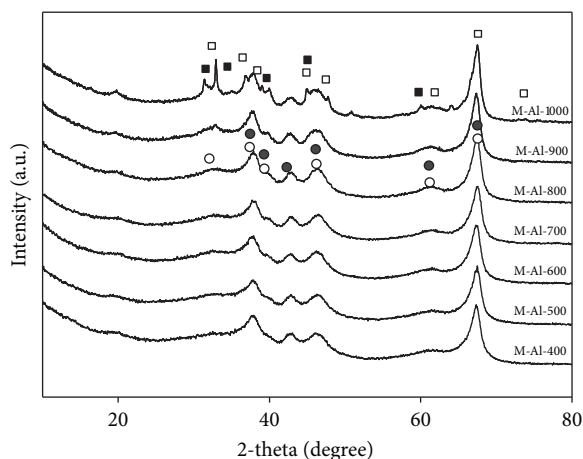


FIGURE 1: XRD patterns of mixed γ - and χ -crystalline phase alumina catalysts with various calcination temperatures; (O) gamma-alumina, (●) chi-alumina, (□) theta-alumina, and (■) delta-alumina.

TABLE 1: BET surface area, pore volume, and pore size diameter of the mixed γ - and χ -crystalline phase alumina.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size diameter (nm)
M-Al-400	233	0.53	5.94
M-Al-500	191	0.54	7.29
M-Al-600	187	0.57	8.09
M-Al-700	157	0.51	8.39
M-Al-800	149	0.51	8.51
M-Al-900	142	0.49	8.98
M-Al-1000	114	0.42	9.41

from 233 to 144 m²/g with calcination temperature from 400°C to 1000°C. The pore volume of alumina catalysts seems to be constant with an increase in the calcination temperature. The M-Al-600 shows the highest pore volume (0.57 cm³/g). All catalysts exhibited increased pore size diameter from 5.9 to 9.1 nm with increasing calcination temperature. It is suggested that an increase in calcination temperature aggregated the catalyst resulting in losing the surface area, increasing the pore sizes diameter, and decreasing the pore volume.

From the previous work, it was suggested that an increase of calcination temperature insignificantly affects the morphologies of mixed γ - and χ -crystalline phase alumina catalysts. However, Pansanga et al. [13] reported the morphology of mixed phase alumina, which was obtained by transmission electron microscopy (TEM) technique. They found that the morphology of alumina with different phases presented different structure. The morphologies of mixed γ - and χ -crystalline-phase alumina exhibited wrinkled sheets and spherical particles of γ - and χ -crystalline phase alumina, respectively.

Figure 2 shows the TEM micrographs of the M-Al-400 and M-Al-1000. It confirms that the obtained catalysts

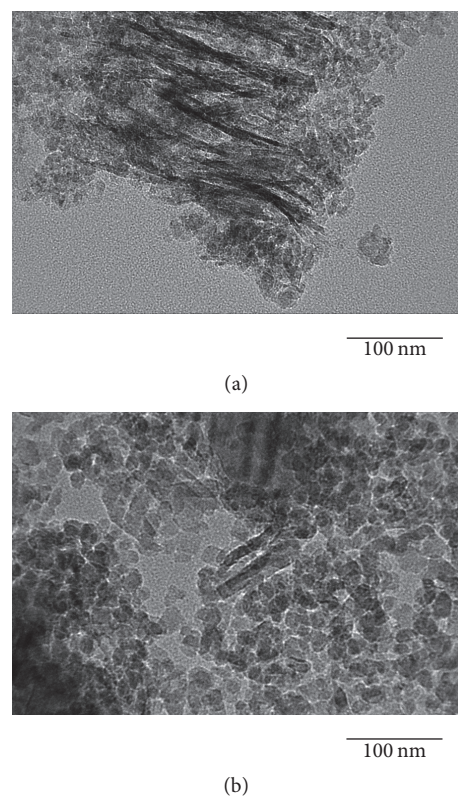


FIGURE 2: TEM micrographs of the (a) M-Al-400 and (b) M-Al-1000.

contain the mixed γ - and χ -crystalline-phase alumina indicating wrinkled sheets and spherical particles, according to Pansanga et al. [13]. The calcination temperature significantly affects the phase transformation as seen from XRD and TEM. Figure 2(a) shows two types of morphologies, which is mixed phase of γ - and χ -alumina calcined at 400°C. When the calcination temperature was increased to 1000°C, XRD suggested that the phase transformation occurred. It was proven by TEM as seen in Figure 2(b) that it appears as spherical particles and scarcely wrinkled sheets. It is suggested that the wrinkled sheets (γ -phase alumina) were transformed to other phase, while the spherical particles (χ -phase alumina) remain unchanged. It is in good agreement with the XRD result as seen for the peaks of M-Al-1000 at 43°. This indicated that χ -phase alumina was still observed. On the other hand, the peaks of γ -phase alumina were observed differently.

The total acidity was significantly decreased with increasing the calcination temperature (Table 2). This is because the hydroxyl group on catalyst surface was released with increasing the calcination temperature, leading to lower acidity. Besides, the total acidity can be divided into two types of acidic sites: weak acid sites and medium to strong acid sites. For weak acid sites, the position of weak acid sites exhibited the amount of NH₃ desorption in the range from 215 to 109 μ mol NH₃/g cat. The M-Al-400 exhibited the highest acidity. However, the position of medium to strong acid sites was presented in the range from 705 to 337 μ mol NH₃/g cat.

TABLE 2: The amount of acidity of mixed γ - and χ -crystalline-phase alumina catalysts with various calcination temperatures.

Sample	NH ₃ desorption ($\mu\text{mol NH}_3/\text{g cat.}$)		Total acidity ($\mu\text{mol NH}_3/\text{g cat.}$)
	Weak	Medium to strong	
M-Al-400	215	489	705
M-Al-500	195	494	689
M-Al-600	148	513	661
M-Al-700	155	387	542
M-Al-800	109	364	473
M-Al-900	172	230	402
M-Al-1000	146	191	337

3.1.2. Reaction Study. The catalytic performance of all catalysts was tested in ethanol dehydration. The reaction was carried out in the temperature ranging from 200°C to 400°C. The catalytic activity depends on the operating temperature, according to previous reports [7, 8, 10]. The results of catalytic activity were reported in terms of conversion and selectivity versus temperature profile. Besides the operating temperature, the catalyst acidity is an important factor influencing the conversion and selectivity of ethanol.

The acidity results are summarized in Table 2. The M-Al-600 exhibited the highest medium to strong acidity, followed by the M-Al-500 and M-Al-400. This result is in agreement with the previous report [17], in which the dehydration of ethanol over acid catalyst was studied and it was found that the products of ethanol dehydration reaction are ethylene (main product), diethyl ether, and acetaldehyde. The ethylene formation is favored by medium to strong acid sites, whereas diethyl ether requires only weak acid sites. At low temperature, diethyl ether is the major product, while, at high temperature, ethylene prevails. For the M-Al-1000, it exhibited the lowest medium to strong acidity.

The ethanol conversion increased with increasing reaction temperature (Figure 3). Similar trend was observed for all catalysts. The M-Al-400, M-Al-500, and M-Al-600 catalysts showed good performance with near complete ethanol conversion. However, at temperature higher than 400°C, deactivation can occur and products can be further converted to other products [16]. Considering the relationship between acidity and ethanol conversion, it was found that the medium to strong acidity plays an important role in the ethanol conversion. At high temperature, the selectivity of ethylene for all catalysts was higher than that at low temperature as shown in Figure 4.

On the contrary, the selectivity of diethyl ether apparently decreased with increasing temperature as seen in Figure 5. This result can be ascribed by thermodynamic properties. The reaction of ethanol to ethylene is endothermic reaction. Thus, it requires high temperature. On the other hand, the reaction of ethanol to diethyl ether is exothermic reaction; therefore diethyl ether is favored at the lower temperature. For the selectivity of acetaldehyde, it is presented in Figure 6. It was found that acetaldehyde selectivity was almost similar for all catalysts except for the M-Al-900 and M-Al-1000. In

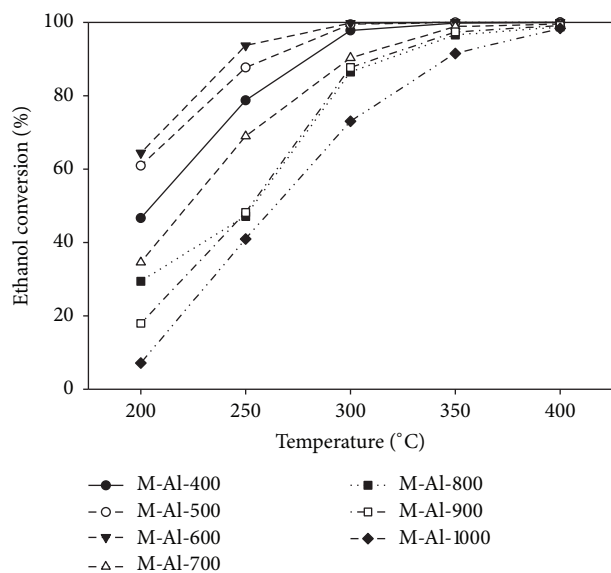


FIGURE 3: Ethanol conversion profiles in ethanol dehydration at different temperatures.

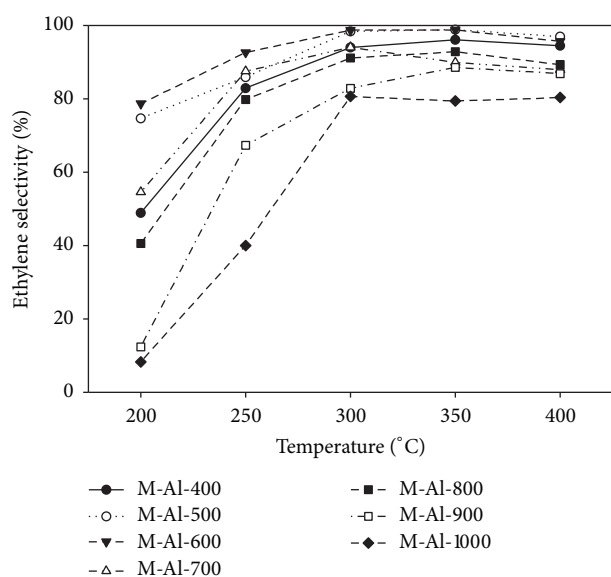


FIGURE 4: Selectivity of ethylene profiles in ethanol dehydration at different temperatures.

summary, the M-Al-600 catalyst shows the highest ethanol conversion (99.98%) and ethylene selectivity of 98.76% at 350°C having the ethylene yield of 98.75% (Table 3) at this temperature.

3.2. Effect of Mo Modification

3.2.1. Characteristics. X-ray diffraction patterns of Mo-modified M-Al-600 catalyst are shown in Figure 7. It can be seen for 5Mo/M-Al-600 and 10Mo/M-Al-600 that no distinguishable peaks of Mo species were observed in XRD

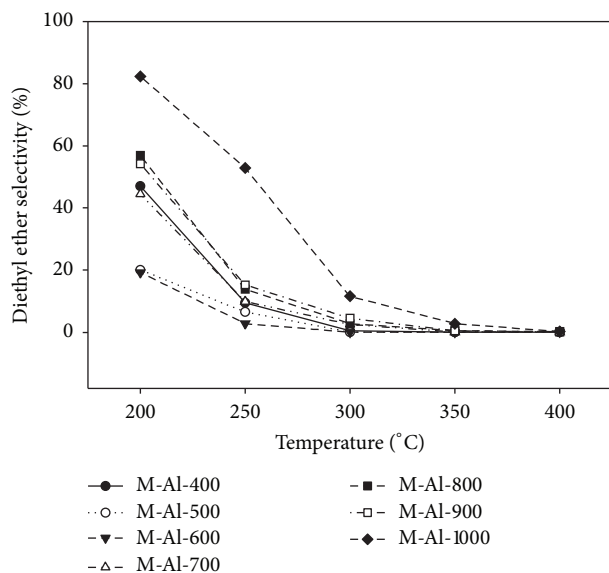


FIGURE 5: Selectivity of diethyl ether profiles in ethanol dehydration at different temperatures.

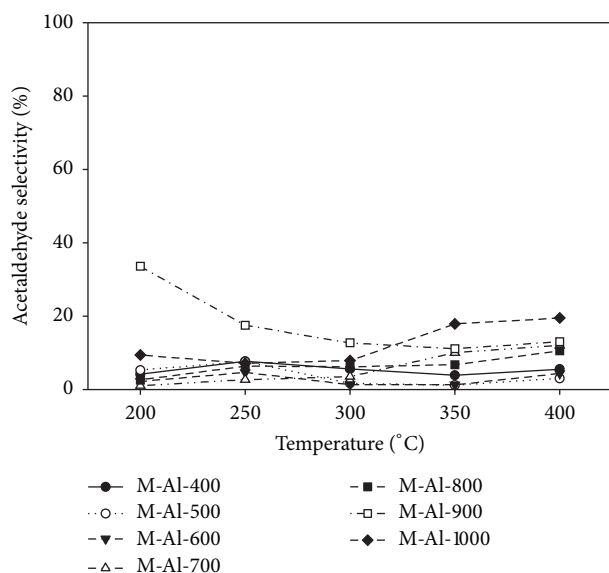


FIGURE 6: Selectivity of acetaldehyde profiles in ethanol dehydration at different temperatures.

TABLE 3: The yield of ethylene of M-Al-600 catalyst.

Reaction temperature (°C)	Ethanol conversion (%)	Ethylene selectivity (%)	Ethylene yield (%)
200	64.38	78.65	50.63
250	93.68	92.59	86.74
300	99.74	98.67	98.41
350	99.98	98.76	98.75
400	100.00	95.57	98.57

patterns. Only XRD peaks for the mixed γ - and χ -crystalline-phase alumina were observed. It indicates that, at low Mo loading (<10 wt%), Mo was well dispersed on alumina surface. The sample with high amount of Mo (15 wt%–20 wt%),

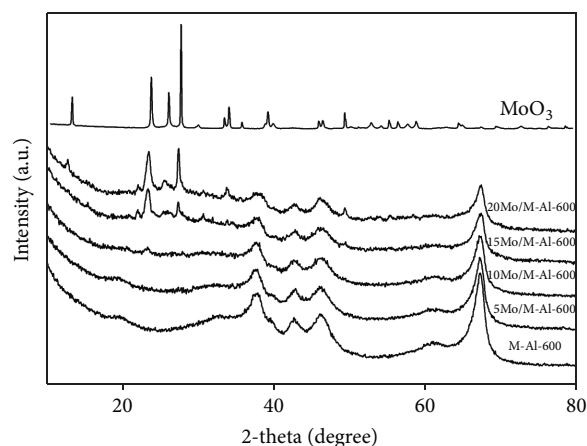


FIGURE 7: XRD patterns of mixed γ - and χ -crystalline phase alumina, MoO_3 -modified alumina, and MoO_3 .

TABLE 4: BET surface area, pore volume, and pore size diameter of the MoO_3 -modified catalysts.

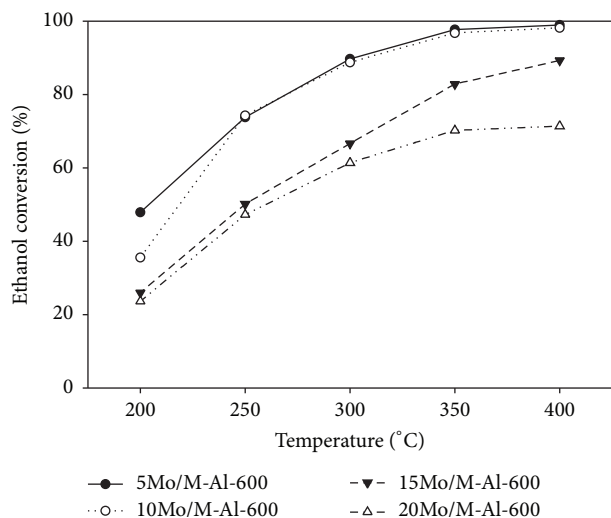
Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size diameter (nm)
M-Al-600	187	0.57	8.09
5Mo/M-Al-600	185	0.45	6.88
10Mo/M-Al-600	164	0.43	7.20
15Mo/M-Al-600	134	0.35	7.12
20Mo/M-Al-600	131	0.35	6.74

showed XRD peaks at 2θ of 27.3° , 25.7° , and 23.3° , which are characteristics of MoO_3 [12]. The intensity of the diffraction peak can be attributed to an increase of MoO_3 species indicating the formation of crystalline MoO_3 on alumina surface.

BET surface area, pore volume, and pore size diameter of Mo-modified catalysts are summarized in Table 4. The BET surface area and pore volume were decreased with an increase of MoO_3 loading. This may be due to the accumulation of the MoO_3 on alumina surface. Although the 5Mo/M-Al-600 and 10Mo/M-Al-600 did not reveal the MoO_3 species, the BET surface area, pore volume, and pore size diameter of both catalysts were decreased. In addition, from Table 4, the impregnation with MoO_3 apparently lowered BET surface area and pore volume of support but did not significantly change the porous structure. The reduction of surface area was caused by blockage of smaller pore by MoO_3 particles, while it did not affect the larger pore. As a result, the average pore size diameter of modified catalyst was not significantly changed. It was in the range of 6.74 to 7.20 nm. This indicated that, at lower loading, MoO_3 was well dispersed on the support surface probably as the monolayer [18]. However, at higher MoO_3 loading (20Mo/M-Al-600), the decrease of the BET surface area and pore volume because the formation of MoO_3 crystallites obstructs the small pores and/or surface of catalysts is clearly seen. The pore size diameter of modified catalyst was in the range of 6.74 to 7.20 nm, which was lower

TABLE 5: The amount of acidity of MoO₃-modified catalysts.

Sample	NH ₃ desorption ($\mu\text{mol NH}_3/\text{g cat.}$)		Total acidity ($\mu\text{mol NH}_3/\text{g cat.}$)
	Weak	Medium to strong	
M-Al-600	148	513	661
5Mo/M-Al-600	289	634	923
10Mo/M-Al-600	249	727	977
15Mo/M-Al-600	220	795	1015
20Mo/M-Al-600	263	851	1114

FIGURE 8: Ethanol conversion profiles in ethanol dehydration of the MoO₃ over mixed γ - and χ -crystalline phase alumina catalysts.

than M-Al-600. This result is due to the covering of MoO₃ crystallites on surface and pore of catalysts.

The total acidity was enhanced explicitly with an increase in the MoO₃ loading (Table 5), especially the medium to strong acid sites ($634 \mu\text{mol NH}_3/\text{g cat.}$ for the 5Mo/M-Al-600 compared to $851 \mu\text{mol NH}_3/\text{g cat.}$ for the 20Mo/M-Al-600). This is suggested that the addition of MoO₃ has a significant effect on the acidity of the mixed phase alumina catalysts. Although, the increased acidity with the MoO₃ loading cannot be identified in terms of Lewis and Brønsted acidity, Heracleous et al. [19] suggested that the new acid sites generated from the introduction of Mo are of Brønsted species, while only Lewis acid sites were identified on the alumina support [20–22].

3.2.2. Reaction Study. The Mo-modified M-Al-600 catalysts with various Mo loadings were tested in ethanol dehydration reaction. The ethanol conversion over different catalysts is shown in Figure 8. It displays the similar trend to the ethanol conversion of the M-Al-600, where it increased with increasing operating temperatures. When comparing the Mo-modified alumina series with the unmodified catalysts (M-Al-600), it was found that the ethanol conversion of modified alumina was lower than that of the M-Al-600, although the modified alumina had more amount of acidity

TABLE 6: Turnover frequency of the acid and Mo sites.

Turnover frequency (s^{-1})	
Acid sites ^a	Mo sites ^b
84.4	4.70×10^{-3}

^aBased on dehydration reaction of ethanol to ethylene of the M-Al-600 at 200°C.

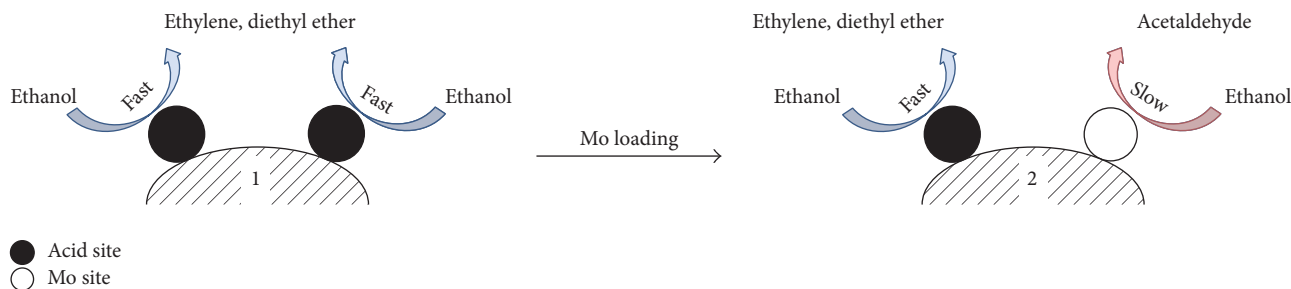
^bBased on dehydrogenation reaction of ethanol to acetaldehyde of the 5Mo/M-Al-600 at 200°C.

than the M-Al-600 catalyst. The reason why the higher total acidity did not render high ethanol conversion can be proposed upon Scheme 1. From Scheme 1, it is assumed that the acid site converts the ethanol molecule faster than the Mo site resulting in ethanol consumption of $1 > 2$. The catalysts without MoO₃ consist of acid sites acting as active phase on surface, while, for the Mo-modified catalysts, some acid sites had taken place by MoO₃. Thus, the surface of catalysts actually contains two types of active phase (acid sites and Mo sites). According to previous study, it suggests that the acid site plays an important role for the dehydration reaction (ethanol to ethylene and diethyl ether). Ethanol was consumed very fast by acid site. In contrast, the Mo sites dominantly acted as the active site for dehydrogenation of ethanol to acetaldehyde. The rate of ethanol consumption was slower than the acid site.

As mentioned above, the ethanol conversion of modified catalyst would be caused from the Mo site. To confirm the rate of ethanol consumption by acid site and Mo site, the turnover frequency (TOF) or turnover number, which describes in the number of molecules reacting per active site per time, was calculated as shown in Table 6.

As seen in Table 6, the TOF of acid site was 84.4 s^{-1} . It means that the 84.4 ethanol molecules were converted to ethylene on each acid site per second. However, only 4.70×10^{-3} molecules of ethanol are converted to acetaldehyde on each Mo site per second. The TOF of acid sites was higher than that of Mo sites. Therefore, when the MoO₃ was added, the acid site and generated new sites (Mo sites) were formed in catalyst. The Mo slowly converted the ethanol molecule resulting in decreasing of overall ethanol consumption.

The selectivity of ethylene, diethyl ether, and acetaldehyde of all catalysts is shown in Figures 9–11, respectively. Both ethylene and diethyl ether selectivity showed the similar trend as seen from M-Al-600 catalysts. Ethylene favors high temperature, whereas diethyl ether requires lower temperature.



SCHEME 1: Ethanol consumption phenomena on active site.

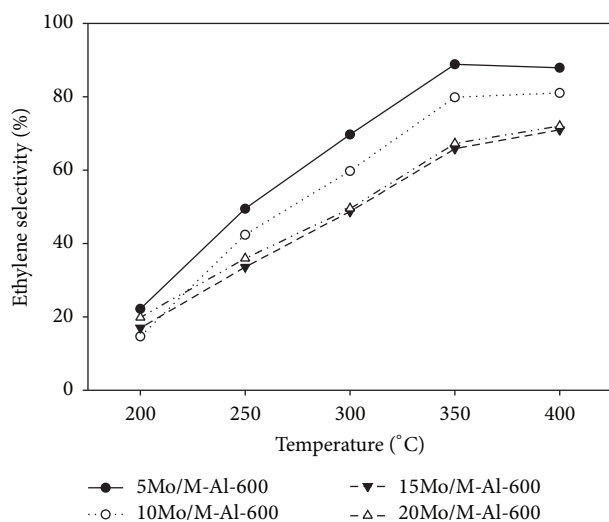


FIGURE 9: Selectivity of ethylene profiles in ethanol dehydration at different temperatures.

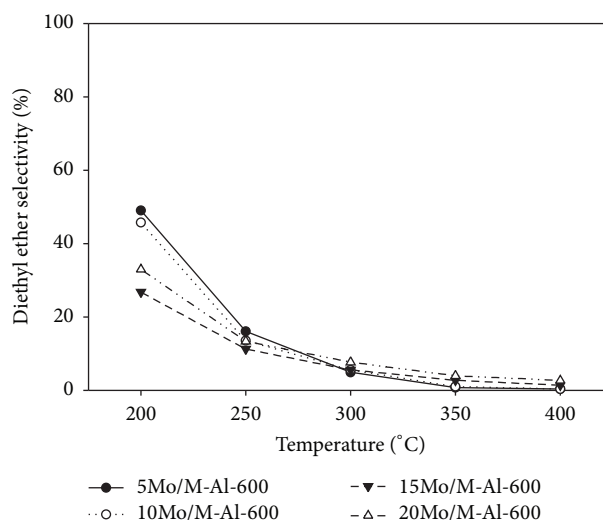


FIGURE 10: Selectivity of diethyl ether profiles in ethanol dehydration at different temperatures.

An enhancement in acetaldehyde selectivity was observed with introduction of MoO_3 . The increase in selectivity of acetaldehyde was due to the fact that Mo species promoted dehydrogenation pathway. The MoO_3 added into the mixed phase alumina substituted the acid sites on catalyst surface, resulting in formation of new sites. This result is corresponding to the NH_3 -TPD data, which explained that the acidity on surface of catalysts consists of two types (conventional acid sites and new sites from Mo species). Ethylene and diethyl ether were produced from the conventional acid sites on catalyst surface, whereas the acetaldehyde results from dehydrogenation reaction generated from Mo species.

The selectivity of ethylene was decreased with an increase of Mo loading as shown in Figure 9. In contrast, the selectivity of acetaldehyde was increased with an increase of Mo loading as shown in Figure 10. Although the 20Mo/M-Al-600 exhibits higher amount of the MoO_3 than the 15Mo/M-Al-600, the selectivity of ethylene is not the lowest or the selectivity of acetaldehyde is not the highest. This was due to the fact that accumulation in catalyst pores was observed when Mo loading is more than 15 wt%. Thus, it leads to loss of Mo species. For the selectivity of ethylene, the 5Mo/M-Al-600 exhibited the highest ethylene selectivity (88.85% selectivity of ethylene at 350°C). However, it was lower compared to

the M-Al-600 (98.76% selectivity of ethylene at 350°C). The 15Mo/M-Al-600 had the highest selectivity of acetaldehyde and the selectivity of acetaldehyde was enhanced up to 56.35% at 200°C. In order to compare the catalyst performance in this study with other researches, the ethanol conversion and ethylene yield of various catalysts are summarized in Table 7. It was found that the mixed phase alumina (M-Al-600) is quite competitive among other catalysts and promising for further study in ethanol dehydration to ethylene.

4. Conclusion

It reveals that the calcination temperature has significant effect on acidity of alumina catalysts. The acidity was decreased with increasing calcination temperature especially for medium to strong acid. Moreover, at 1000°C, the mixed γ - and χ -crystalline phase alumina catalysts exhibited significant phase transformation. γ -phase was transformed, while χ -phase remains stable. In the ethanol conversion reaction, both ethanol conversion and ethylene selectivity depend on medium to strong acid. In this study, the mixed γ - and χ -crystalline phase alumina catalyst, which was calcined at 600°C (M-Al-600), exhibited the highest catalytic activity. It shows the highest ethylene yield of 98.75% at 350°C. In

TABLE 7: Comparison of catalytic activity of various catalysts for ethanol dehydration to ethylene.

Catalyst	Reaction temperature (°C)	Ethanol conversion (%)	Ethylene yield (%)	Ref.
M-Al-600	350	99.98	98.75	This work
5Mo/M-Al-600	300	97.64	86.75	This work
Fe/Al ₂ O ₃	350	75.2	34.29	[9]
Fe ₂ O ₃	350	82.18	28.76	[10]
Mn ₂ O ₃	350	68.16	15.00	[10]
Fe ₂ O ₃ /Mn ₂ O ₃ (1:1)	350	76.00	30.40	[10]
TiO ₂ /γ-Al ₂ O ₃ (microreactor)	360–550	95–99.96	91–99.30	[11]
SiO ₂	350	2.5	0.89	[23]
MgO-Al ₂ O ₃	350	11.2	4.62	[23]
ZrO ₂	350	45.4	36.00	[23]
TiO ₂	350	80.1	11.29	[23]
Commercial Al ₂ O ₃	450	85	66.90	[24]

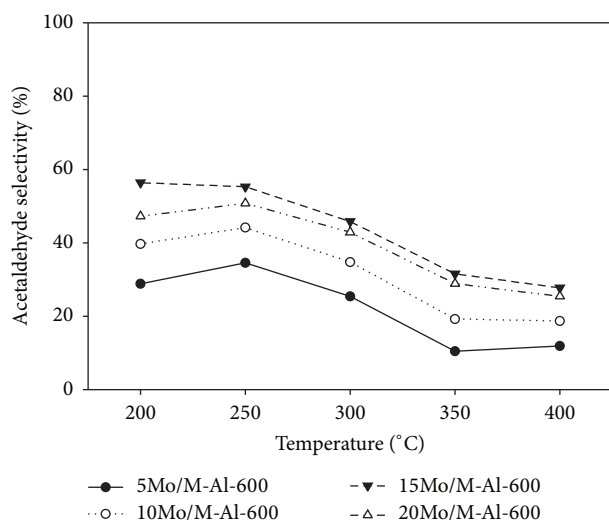


FIGURE 11: Selectivity of acetaldehyde profiles in ethanol dehydration at different temperatures.

addition, with Mo modification, it was found that enhancement of acetaldehyde was observed. However, it is proposed that the active site to produce acetaldehyde was much lower compared with those to produce ethylene.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

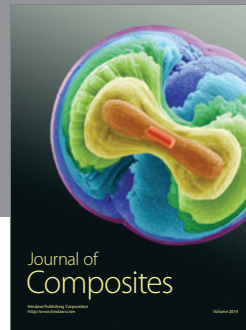
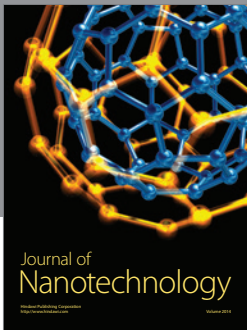
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