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Indonesian Montmorillonite-supported ZnO: Preparation, Characterization and Activity Test in Methanol Dehydration

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ABSTRACT

In this study, a composite of montmorillonite-supported ZnO (ZnO/MMT) prepared from Indonesian montmorillonite, characterization and activity test evaluated in methanol dehydration reaction was conducted. Material preparation was performed by using sol-gel dispersion of ZnO from zinc acetate precursor into suspension of acid-activated montmorillonite followed by drying and calcination. Effect of structural modification towards physico-chemical character such as surface acidity, crystallinity, specific surface area, porosity and also surface morphology was investigated. For surface acidity analysis, n-butylamine adsorption procedure followed by FTIR analysis was utilized while x-ray diffraction (XRD), BET surface area analysis and SEM were employed to evaluate crystallinity, specific surface area and also surface profile, respectively. Correlation of physico-chemical properties with catalytic activity in methanol dehydration reaction was analyzed. Significant increase in total surface acidity and Lewis acid to Brønsted acid ratio as important factor affecting catalyst activity to convert methanol to dimethyl ether as main product was gained by composite preparation. Comparative kinetics study of catalyzed reaction suggested the physico-chemical character dependent as representative heterogeneous mechanism involved in the methanol dehydration reaction in that ZnO/MMT exhibited the higher rate of methanol conversion.

Key words: Montmorillonite, supported metal oxide, methanol dehydration, surface acidity

INTRODUCTION

Dimethyl Ether (DME) has been receiving a growing attention as a chemical product having potential advantages in the diminution of global environmental pollution and clean energy supply and also can be derived from renewable resources. Due to its high cetane number (55-60), no release of sulfur compounds, lower NO_x emission, less smoke and engine noise compared with those of traditional diesel fuels, DME is a clean alternative diesel fuel. Dehydration of methanol is one of several alternatives to produce dimethyl ether, valued as the most favor step and economically reasonable (Tock *et al.*, 2010; Lei *et al.*, 2011).

An efficient and environmental-friendly of methanol dehydration was reported by using solid acid catalyst such as silica-alumina classes (Xu *et al.*, 1997; Lee *et al.*, 2005; Keshavarz *et al.*, 2010). Reaction is driven by carbocation stabilization over high specific surface area and stability while carbocation formation is the rate-determining step in the mechanism. Refer to previous works, chemisorption of methanol on surface to produce methoxonium ion of H_3COH_2^+ during mechanism can be achieved by the combination of Brønsted and Lewis acid sites (Kim *et al.*, 2008). Surface acidity correlated with porous structure is also gained from clay and pillared clays utilization (Bandiera and Naccache, 1991). Clay material is specified as material having high surface area and due to its adsorptivity towards some molecules, it potentially utilized for this purpose (Fan *et al.*, 2006; Fatimah *et al.*, 2009; Wibowo *et al.*, 2011; Ekosse and Mulaba, 2008). Montmorillonite is a kind of clay in the class of smectite and generally called as bentonite in the tradename. Several researches investigated the potency of bentonite or montmorillonite as adsorbent in chemisorption mechanism significantly for heavy metal and hydrocarbon also the modified montmorillonite as solid support of heterogeneous catalyst (Fatimah *et al.*, 2009; Al-Jilil, 2010; Al-Jilil and Alharbi, 2010; Gitipour *et al.*, 2006). Structurally, montmorillonite containing silica-alumina sheets framework in 2:1 ratio and its porous structure is accessible to conduct adsorption respect to a reactant in a specific reaction. The presence of proton created from silica-alumina and the possible replacement of metal in framework should form surface acidity of high but refer to heterogeneity content as natural resource, its stability will easily loose in high temperature (Kpangni *et al.*, 2008; Wibowo *et al.*, 2011; Hoidy *et al.*, 2010; Yssaad and Belkhodja, 2007). Clay modification through metal oxide pillarization and supporting metal oxide is feasible method to repair this limitation (Laredj *et al.*, 2008; Fatimah *et al.*, 2009). Increased catalytic activity regarding to increased surface profile and acidity was pointed out from several reactions such as esterification, hydrocracking and selective catalytic reduction. In this research, dimethyl ether from methanol dehydration reaction was tried to be produced by using a composite catalyst of montmorillonite-supported ZnO (ZnO/MMT). Effect of ZnO immobilization targetted in the synthesis is acidity created on surface and play role in dehydration mechanism as reported in its immobilization over Allophane (Ghoneim *et al.*, 2007). Kinetics study of the reaction and also catalyst effect to the product selectivity was investigated by measure the conversion of methanol as a function of time on comparing the use of ZnO/MMT and raw montmorillonite. Role of modification to the material physicochemical character and activity towards methanol dehydration is main focused in the study.

MATERIALS AND METHODS

Natural montmorillonite was received from PT. Tunas Inti Makmur, Semarang, Indonesia. The chemical composition of montmorillonite is reported (Fatimah *et al.*, 2011); SiO_2 62.411%, Al_2O_3 13.273%, Fe_2O_3 4.772%, MgO 4.551%, CaO 2.555%, Na_2O 0.038% and K_2O 0.090%. The cation exchange capacity is within the range of 68-86 meq 100 g^{-1} . It was chemically activated by refluxing in acid solution with the same detail procedure before used as parent material (Fatimah *et al.*, 2011). Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$); sodium hydroxide (NaOH), methanol and isopropanol in pure analyst grade were purchased from E. Merck.

Material preparation: ZnO precursor was prepared by dilluting zinc acetate dihydrate in water: Isopropanol under strong stirring for 1 h in a basic environment. Dispersion of ZnO into montmorillonite was prepared by addition of ZnO precursor into suspension of activated

montmorillonite droply until a theoretical Zn content of 5% wt. was gained. Further steps were stirring the mixture for a night, filtration and calcination at 500°C. Particularly, preparation procedure of ZnO dispersion in this research was different with as reported in the past research (Fatimah *et al.*, 2011) in which pre-intercalation procedure towards montmorillonite structure by using surfactant was not employed. Material obtained from the synthesis process is characterized by XRD, BET specific surface area and SEM-EDX spectroscopy. Surface Brensted acidity was measured by butylamine titration while Lewis to Bröensted acid ratio (LB^{-1}) was examined by pyridine adsorption followed by Fourier-Transform Infra Red spectroscopy (FTIR) analysis. Profile of catalyst material can be predicted through XRD and spesific surface area analysis as reported from previous research (Dhanapandian and Gnanavel, 2009; Fatimah *et al.*, 2009). Activity test of material in methanol dehydration was tested in a fixed bed reactor. The reactor was a cylindrical tube, 25 mm internal diameter and 0.4 m high placed in a thermo controlled tubular furnace and connected to feed section. Methanol vapor was feeded into reactor filled with powder catalyst with the carrier gas (N_2) after setting the reactor temperature. For kinetic study, analysis to a part of exit gas at certain times was carried out by gas chromatography-mass spectrometry (GCMS) apparatus (Shimadzu). Methanol conversion and product selectivity to dimethyl ether are is defined by following equation (Eq. 1, 2):

$$\text{Conversion (\%)} = \frac{[\text{MeOH}]_0 - [\text{MeOH}]_t}{[\text{MeOH}]_0} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{[\text{Dimethylether}]}{[\text{Total product}]} \times 100 \quad (2)$$

RESULT AND DISCUSSION

Figure 1 illustrates the XRD pattern of raw montmorillonite and ZnO/MMT.

Montmorillonite diffractogram shows the specific reflection at $2\theta = 6.3^\circ$ ($d_{001} = 14.9\text{\AA}$) and other refections 19.89 and 35.6° corresponding to d_{020} and d_{006} , respectively. These peaks are in consistence

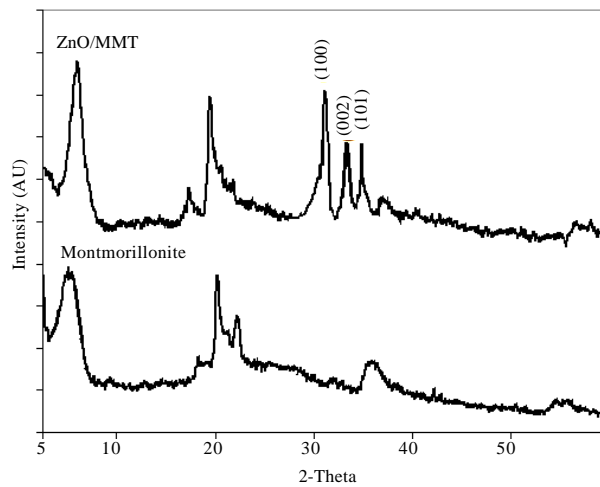


Fig. 1: XRD profile of montmorillonite and ZnO/MMT

with as reported in previous research indicating the structure of Na-montmorillonite and analogues to the XRD patterns reported by Sarier *et al.* (2010) and De Stefanis and Tomlinson (2006). After it was dispersed with ZnO, the pattern of ZnO/MMT showed the presence of some new peaks correspond to the ZnO formation identified in ZnO/MMT. These peaks are the reflection at 31.8; 32.6 and at 36.3 correspond to (100) (002) and (101) reflections. These peaks are correspond observation reflects the presence of wurzite phase of ZnO (Singh *et al.*, 2008; Sharma *et al.*, 2010). The occurrence of these peaks while these were absent in previous preparation is caused by the higher content of Zn in composite preparation. The presence of ZnO particles formation in material is also showed by the surface profile obtained from SEM and elemental analysis performed by EDX listed in Table 1.

From Fig. 2, ZnO/MMT described the characteristics aggregates attached on montmorillonite surface. The morphology of distributed form is similar with what was reported by Bahadur *et al.* (2007) indicate the chrystal growth by sol-gel synthesis method. Effect of ZnO attachement in montmorillonite matrix to the surface profile and pore distribution is studied by N₂ gas sorption analysis.

Data of specific surface area, pore volume and pore radius based on BET isotherm analysis is tabulated in Table 1. It is noted that gas sorption analysis showed the increased specific surface area of montmorillonite after the dispersion suggested the formation of metal oxide porous structure on montmorillonite surface by zinc oxide formation accessible for N₂ gas to be adsorbed.

Table 1: Surface parameter from BET surface area analyzer

Sample	Specific surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore radius (Å)
Montmorillonite	48.60	0.038	15.92
ZnO-MMT	92.47	0.021	10.25

Table 2: Measured total acidity and Lewis to Bronsted acid ratio

Sample	Total acidity (mmol butylamine g ⁻¹)	LB ⁻¹
Montmorillonite	0.65	0.85
ZnO/MMT	1.95	0.97

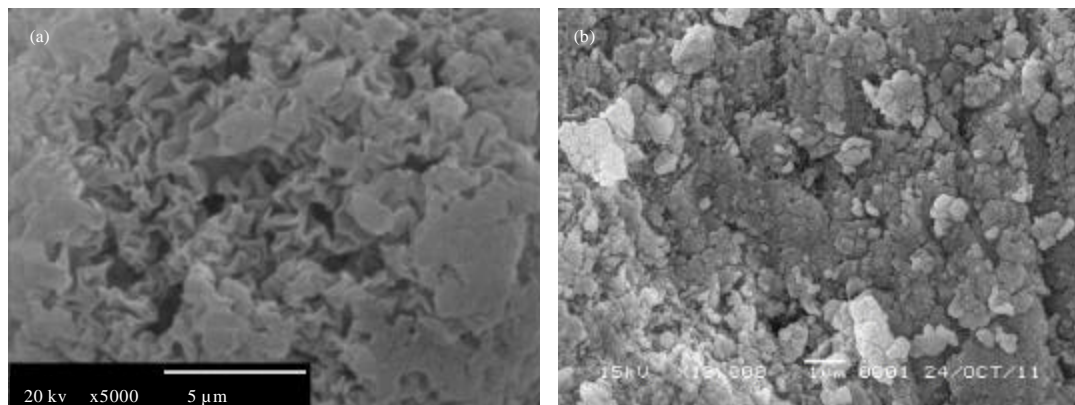


Fig. 2(a-b): SEM profile of (a) raw montmorillonite (b) ZnO/MMT

Table 3: Selectivity of products on varied temperature

Temperature (°C)	Selectivity on ZnO/MMT catalyst (%)			Selectivity on montmorillonite catalyst (%)		
	HC	CO ₂	DME	HC	CO ₂	DME
200	0	0.05	99.95	0	0	100
300	0	0.09	99.91	0	0	100
400	0.099	0.12	99.88	0	0.1	99.9

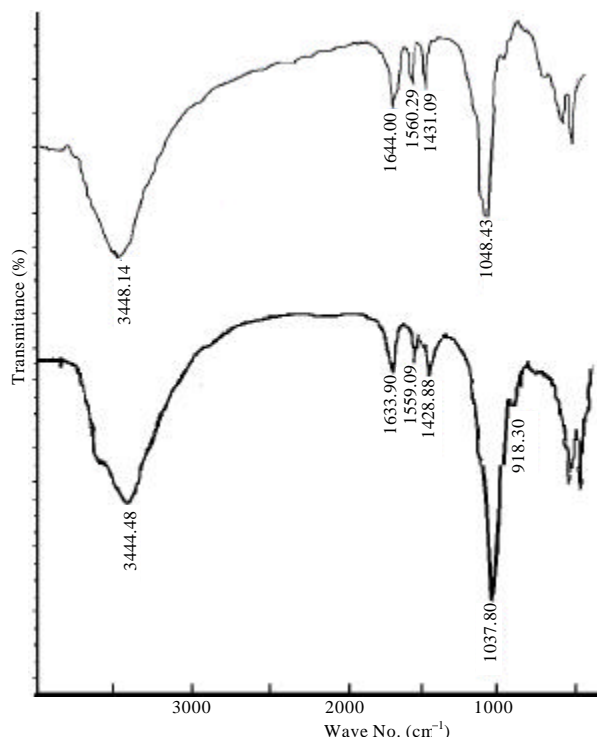


Fig. 3: FTIR spectrumm of pyridine-adsorbed montmorillonite (above) and ZnO/MMT

Character of surface acidity as main factor affecting the mechanism in methanol dehydration was studied by identifying Lewis to Bronsted surface acidity (LB^{-1}) from the experiment of pyridine adsorption followed by FTIR analysis (Table 2). As reported by previous researches, ammine compounds were utilized as probe molecule in determining surface acidity of some solids (Roy *et al.*, 2005; Khan *et al.*, 2009). Pyridine is a probe molecule for both acids whereas adsorbed aromatic ring of the structure can be used as identity of the Brønsted protons and recorded ammine functional group marked from Lewis acid sites. The compared spectra is depicted in Fig. 3 and calculated LB^{-1} ratio (refer to equation) and total acidity measured by butylamine titration method is presented in Table 3. Figure 3 and the tabulated data expressed the increased total acidity evaluated from n-butylamine method as well as increased Lewis acid sites created after modification of montmorillonite using ZnO as shown by higher value of LB^{-1} ratio. Dispersed ZnO particles on surface provides the Lewis acid sites competence to interact with ammine group in butylamine.

$$LB^{-1} = \frac{I_{1450-1455} \text{ cm}^{-1}}{I_{1540-1560} \text{ cm}^{-1}}$$

The spectra of both ZnO/MMT and raw montmorillonite after pyridine adsorption shows the characteristics spectrum at around 1037.80 cm^{-1} for montmorillonite associate with the spectrum at 1048.43 cm^{-1} for ZnO/MMT and strengthened by spectra at around $662\text{-}665\text{ cm}^{-1}$ correspond to the presence of Si-O bond. Wide spectra at around $3444\text{-}3458\text{ cm}^{-1}$ in both samples are assigned as the presence of hydroxyl group in clay's framework. By these spectra, it is noted that there is a shift of the spectra to higher wavenumber for ZnO/MMT compared to raw montmorillonite due to ZnO attachment in clay's structure caused higher energy of vibration required. The characteristics band from pyridine adsorption are shown by the spectra at $1428\text{-}1550\text{ cm}^{-1}$ in which the spectra at around $1540\text{-}1550\text{ cm}^{-1}$ are identified from interaction between brønsted acid sites with surface while at 1430 cm^{-1} are correlated with pyridine physisorption interaction of Lewis acid sites with surface. The ratio of brønsted to Lewis acid distribution on surface was calculated based on equation as reported by previous.

Catalytic activity of ZnO/MMT in methanol dehydration: Catalytic activity of ZnO/MMT in methanol dehydration is tested based on Kinetics experiments carried out in a fixed bed reactor. Methanol was feed into catalyst loaded reactor by N_2 gas carrier with flow rate of 20 mL min^{-1} at varied temperature of 200, 300 and 400°C . Comparison on catalyst activity of raw montmorillonite and ZnO/MMT is displayed by methanol conversion and selectivity of DME of the reaction (Fig. 4).

It is noted that ZnO/MMT gives better performance in methanol conversion compared to raw montmorillonite at all temperature. The profile is in relation with the physico-chemical character of material specifically from the improvement of solid surface acidity. The presence of Brønsted and Lewis acid sites of prepared material facilitates the interaction between methanol and surface more intensively so the faster reaction occurred during alcohol dehydration mechanism (De Stefanis and Tomlinson, 2006). From varied temperature, a different pattern of methanol conversion is shown by an elevated followed by a relative constant value of the conversion (at 300 and 400°C) on montmorillonite utilization while by using ZnO/MMT the conversion was relative constant and it tends to decrease at 400°C . The lower conversion at 400°C probably ascribe to catalyst deactivation at elevated temperature and also correlated with the potency of coke formation. This assumption is also indicated by selectivity of product at varied temperature listed in Table 3.

Selectivity to DME product over ZnO/MMT catalyst is decreased on elevated temperature while CO_2 and HC products increased. The detected hydrocarbon in the product is assigned to selectivity

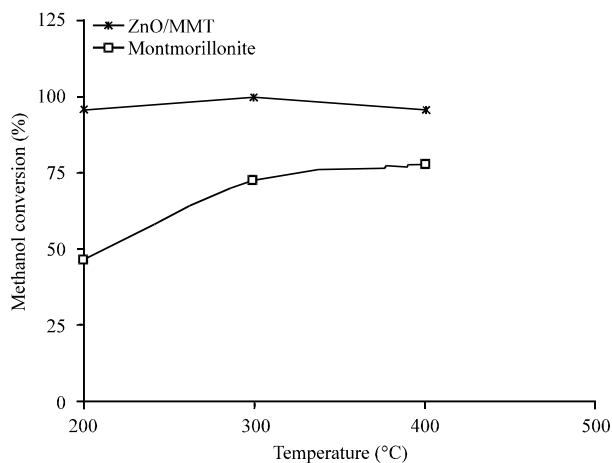


Fig. 4: Methanol conversion by using raw montmorillonite and ZnO-montmorillonite catalyst

reduction correlate with higher acid distribution of the surface. Similar consideration was used by Mishra and Parida (2006) related to improvement of catalytic activity of surface modified iron-chromium pillared clay in hydrocarbon conversion to dimethyl ether.

CONCLUSION

ZnO/MMT was successfully prepared from natural montmorillonite with increased physico-chemical character regarding to its application as heterogeneous catalyst of methanol dehydration mechanism. Kinetics study shows the role of ZnO/MMT to improve methanol conversion compared to raw montmorillonite and it is noted that effect of temperature to the kinetics is in line with theoretically stated in which increased temperature produce in increased reaction rate.

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