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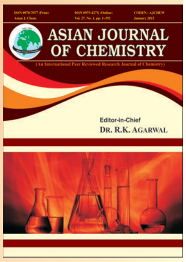

# Synthesis and Application of Alumina Pillared Bentonite Catalyst for Esterification of Acetic Acid with Different Alcohols

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The synthesis of alumina pillared bentonite using $Al_{13}$ Keggin ion pillaring agent has been carried out. We studied their properties and catalysis application for esterification reaction. Characterization studied were performed by using X-ray fluorescence, X-ray diffraction, transmission electron microscopy, BET/$N_2$ gas sorption analysis methods besides the characterization on surface acidity by pyridine adsorptions and FTIR spectroscopy analysis. The experimental results indicated that significant improvement on bentonite physico-chemical characteristics was obtained by a pillarization process using oxide of aluminium. Catalytic activity test showed that $Al_2O_3$ pillared bentonite resulted in higher ethyl acetate percentage relative to the raw bentonite by value of 16.74 and 8.61 %, respectively, although raw bentonite surface acidity was higher than $Al_2O_3$ pillared bentonite. It was demonstrated also that catalytic activity of alumina pillared bentonite was not only affected by surface acidity but also was affected by physico-chemical character of surface *i.e* specific surface area and total pore volume. The effect of alcohols on catalytic activities in esterification reaction was measured using different alcohols consist of methanol, ethanol and *n*-propanol with similar reaction condition for all experiments. Analytical data showed that the conversions of acetic acid by using methanol, ethanol and *n*-propanol were 48.42, 57.89 and 64.20 %, respectively and their selectivities were 100 % for all alcohols.

**Keywords: Bentonite, Pillared clay, Heterogeneous catalyst, Esterification.**

## INTRODUCTION

Esterification is an important reaction in organic chemistry used extensively for synthesis of esters from alcohols and carboxylic acid groups. These ester products include environmentally friendly solvents, flavors, pharmaceuticals, cosmetics, polymerization monomers and emulsifiers in the food and chemical industries[1]. Esterification reaction occurring without catalyst is extremely slow and requires several days to reach equilibrium at the typical reaction conditions. Catalyst often used to increase the rate of reaction in chemical process. Homogeneous catalyst such as hydrofluoric acid, sulfuric acid were reported active as catalyst in esterification reaction. Although these mineral acid catalyst are very effective but it produces highly corrosive media with chemically reactive substances. Purification can be both difficult and hazardous when used to catalyze a chemical process[2]. Recently heterogeneous catalyst has attracted considerable attention of material researchers due to some advantanges of the catalyst such as stable, highly selectivity, reusable, purification is simple and cheaper. The general operation of chemical process is safer and more environmentally friendly[3,4]. Many heterogeneous catalyst such as clay minerals, exchange resin, zeolites, amorphous silica-alumina have been reported to be active in esterification reactions[5-8].

Pillared clays are new class of microporous material with high surface areas which have been extensively studied as interesting material in catalysis application and adsorbents. Performance of these materials can be enhanced by pillaring process to produce high acidity, surface area, porosity and thermal stability. Pillaring is achieved by the insertion inorganic metal polyoxycation in interlayer space of clay structures in order to keep them apart. A calcinations process converts cation in interlayer structure of clays into metal oxide pillars which are responsible for the higher surface area and acidity[9,10]. Alumina pillared clays are the most intensive prepared material compared to the other transition metals possible to be used in pillarization *i.e.* Zr, Cr and Fe[11,12]. The performance of pillared clays as heterogeneous catalyst was affected to surface acidity, catalyst active sites and thermal stability[13,14]. The surface acidity on pillared clays consist of Brønsted acidity is mainly from the layer structural hydroxyl groups, while Lewis acidity is attributed to the metal oxide pillars. In addition, the amount and strength Brønsted and Lewis sites are closely related to the types of clays and metal oxide pillars. Beside that, the performance of pillared clays catalyst is often influenced by the acidity and the porous properties of pillared clays and is also closely related to the type of organic reactants. Size matching between the organic compounds and the pore dimension in pillared clays becomes important for catalysts, as this will determine both the overall yield and selectivity[15].

In this work, synthesis and characterization of alumina-pillared bentonite catalyst for esterification reaction was studied. As reported, some parameters affect the catalytic activity of pillared clays[3,9]. In this study, the effect of alcohol to catalytic activity pillared clays on the esterification reaction is focused. Characterizations using XRD, BET, TEM were, respectively used to determine crystallinities, interlayer distance of clay structures, specific surface area and total pore volume. Surface acidity as an important property was studied by pyridine adsorption methods.

## EXPERIMENTAL

Chemicals used in this research were NaOH, $H_2SO_4$, $AlCl_3·6H_2O$, methanol, ethanol, *n*-propanol, acetic acid in pro analyst grade which were purchased from E. Merck.

**Pre treatment of materials:** Bentonite samples was washed and solid was separated from the slurry. The solid was dried in oven for 6 h.

**Preparation of catalyst:** Keggin ion $Al_{13}$ pillaring agent was obtained by slow titration of NaOH into $AlCl_3·6H_2O$ solution under vigorously stirring until the ratio of OH/Al was equal to 2.2 was reached. The solution was kept overnight and dispersed slowly into 2 % clays suspension in water. The mixture was kept under stirring at room temperature for 24 h and then solid was separated from slurry by filtration and neutralization. Such as process was proceeded by countinous rinsing of the suspension with water until the filtrate had been free from $Cl^-$ (tested by $AgNO_3$ solution). Finally, solids obtained from this step was dried and calcined at 500 °C.

**Characterization of catalyst:** The elemental analysis of the bentonite and pillared bentonite was performed using X-ray flourescence (XRF). The X-ray diffraction data were obtained by XRD Multifex Rigaku with Ni-filtered Copper $K_\alpha$ radiation of wavelength 1.5406 Å, operated at 40 kV and 30 mA. Nitrogen gas sorption analysis for BET isotherm analysis was performed by Quantachrom Autosorb-1. Transmission electron microscopy (JEOL JEM-1400) was used to observe the surface morphology of the bentonite samples. Surface acidity of materials was analyzed by pyridine adsorptions followed by FTIR measurement. 0.5 g of sample was dried in oven for 2 h to overnight exposure of pyridine vapor. In quantitative, adsorbed pyridine was weighted by microbalance samples indicating the strength of acidity. The Brønsted and Lewis distribution was measured by FTIR (as KBr pellet) using Shimadzu Prestige-21 series FTIR spectrometer.

**Catalyst activity test:** Catalytic activity of prepared pillared bentonite was examined by esterification reaction. The reaction was carried out in a three-neck glass reactor (250 mL) fitted with condenser and a thermometer. Alcohol solvent (methanol, ethanol, *n*-propanol) and examined catalyst [1 % (w/v)] were placed in the reactor and heated. Once the reflux temperature of alcohol was reached, acetic acid was added slowly through pipette. About 5 mL of the reaction mixture was taken immediately using pipette and titrated against NaOH solution using phenolphthalein. The concentration of acetic acid consumed during the reaction was calculated by the formula below[16].

$$\text{Concentration of acetic acid (M)} = \frac{C_{NaOH}(M) \times V_{NaOH}\ (mL)}{V_{CH_3COOH}(mL)}$$

where

$C_{NaOH}$ = Concentration of sodium hydroxide (M)

$V_{NaOH}$ = Volume of sodium hydroxide used in titration ($dm^3$)

$V_{CH_3COOH}$ = Volume of reaction mixture sample titrated measures ($dm^3$)

The percentage conversion of acetic acid was equally calculated by the formula below (Fatimah *et al.*[9])

$$\text{Conversion of acetic acid (\%)} = \frac{[Ac]_0 - [Ac]}{[Ac]_0}$$

With:

$[Ac]_0$ = Concentration of acetic acid (M)

[Ac] = Concentration of acetic acid measured (M)

## RESULTS AND DISCUSSION

The XRD pattern of the raw, Al-intercalated and Al-pillared bentonite in the $2\theta = 70°$ range is represented in Fig. 1. The XRD pattern of the raw bentonite showed higher intensity then corresponding intercalated and pillared clay. This could be as a result of ion exchange between the aluminium ion and the native ion on the clay interlayer. The d-spacing for the aluminium-intercalated bentonite is 19.1 Å. The d-spacing for the aluminium-pillared bentonite calcined at 500 °C is 18.2 Å. The major reflection of $d_{001}$ showed a slight shift toward lower angle (2θ) indicating an increase in *d*-spacing as a result of $Al_2O_3$ intercalation into layer space in bentonite.

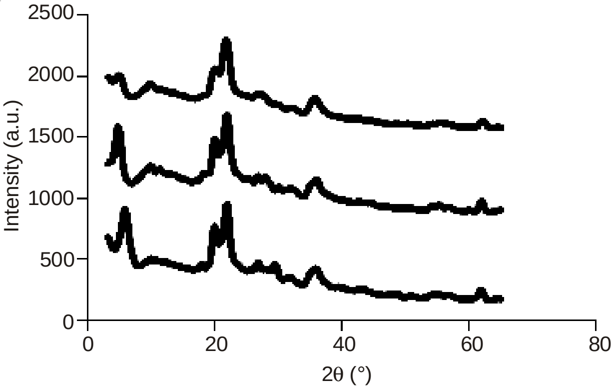

Fig. 1. XRD pattern of (a) raw (b) Al-intercalated (c) Al-pillared bentonite

**Textural properties of Al-pillared bentonite:** Fig. 2 presented the TEM profile of the raw bentonite and Al-pillared bentonite. Increasing of basal spacing in layered structure was

TABLE-1
SPECIFIC SURFACE AREA CALCULATED BY BET ISOTHERM AND *t*-PLOT

| Sample | Specific surface area ($m^2/g$) | Micropore surface area ($m^2/g$) | Pore volume (mL/g) | Average pore radius (Å) |
|---|---|---|---|---|
| Bentonite | 67.531 | 49.761 | 0.164 | 48.45 |
| Al-pillared bentonite | 171.463 | 62.324 | 0.224 | 26.18 |

observed in pillared samples compared to the raw bentonite (Fig. 2). It has indicated the pillar formation within the structure. The effect of pillarization to the BET surface area and porosity is given in Table-1. Changing in BET specific surface areas, pore volume and pore radius of materials are presented as the effect of pillarization.

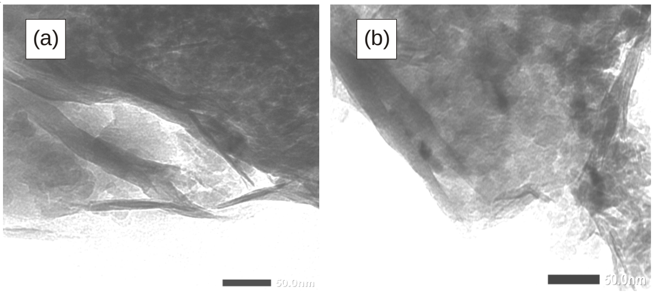

Fig. 2. TEM profile of (a) raw (b) Al-pillared bentonite

Table-1 showed that the specific surface areas and pore volume increasing after pillarization bentonite with aluminium. An increase in the specific surface area is not accompanied by a rise in the average pore radius. This is due to the formation of molecular aggregates aluminium in interlayer or $Al_2O_3$ oxide particles cover the outer surface and cavities from in the bentonite. The adsorption-desorption profile of raw and Al-pillared bentonite demonstrated in Fig. 2

Fig. 3 show that there has been a change in the pattern of adsorption-desoprtion isotherms after pillarization process. This change in the pattern of adsorption isotherms showed an increasing adsorption capacity as a result of an increase in the specific surface area and total pore volume on Al-pillared bentonite (Table-1). Pore distribution in Al-pillared bentonite contained a dominant pore distribution in the radius range of around 28.109 Å (Fig. 4). According to IUPAC definition, such pores are layed at mesoporous range (diameter of 20-500Å in size).

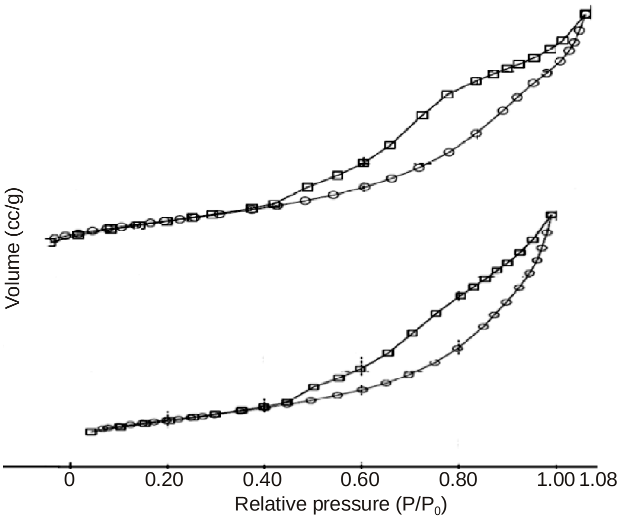

Fig. 3. Adsorption-desorption profile of (a) raw (b) Al-pillared bentonite

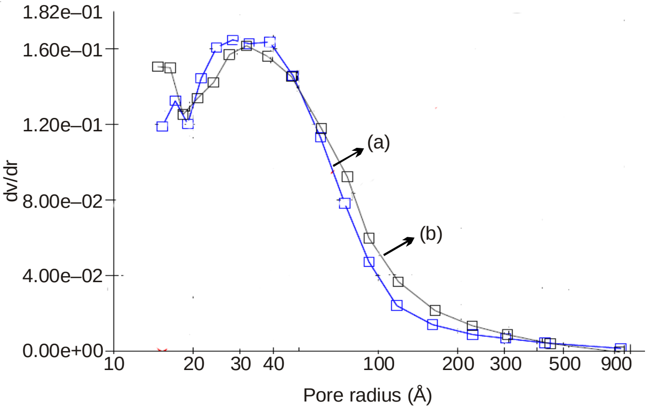

Fig. 4. Pore size distribution of (a) raw (blue) and (b) Al-pillared bentonite (black)

**Surface acidity properties of Al-pillared bentonite:** The property of surface acidity in pillared materials is a required character in most catalytic applications such as in esterification reaction. Brønsted and Lewis acid sites distribution in surface are measured by pyridine adsorption treatment to materials followed by FTIR analysis to the pyridine adsorbed samples. Vibration spectra of pyridine are shown at range of 1700-1400 $cm^{-1}$. Vibration spectrum at 1560-1540 $cm^{-1}$ is related to the Bpy sites and the spectrum at the range of 1455-1450 $cm^{-1}$ is characteristic for Lpy sites[13]. FTIR spectra of raw bentonite and Al-pillared bentonite after pyridine adsorption treatment are given in Fig. 5.

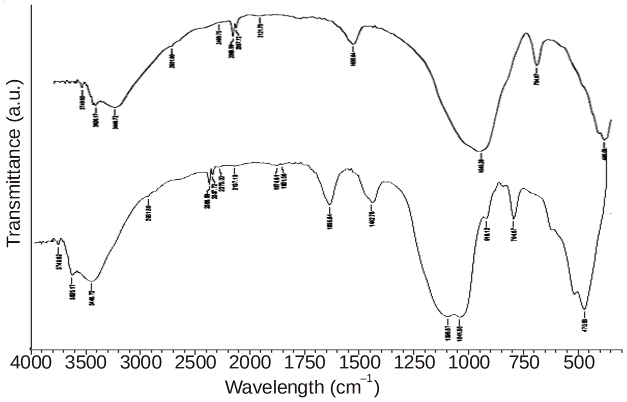

Fig. 5. FTIR spectrum of pyridine adsorbed (a) raw bentonite (b) Al-pillared bentonite

**FTIR spectra show similiarties of some peaks:** Vibration around 1041.56 $cm^{-1}$ which attributed to Si-O stretching asymmetric vibration. Intense band at around 3448.72 $cm^{-1}$ are indication of skeletal hydroxyl group in clay structure. The vibration around 794.56 $cm^{-1}$ attributed to Si-O stretching symmetric vibration and vibration around 470.63 $cm^{-1}$ attributed to Al-O bond. It can be noticed from raw bentonite and Al-pillared bentonite is the shift of vibration to Al-O and Si-O bands to the higher wavenumber. This suggest that $Al_2O_3$

intercalation to clay structure gives higher vibrational energies. The Brønsted acid sites are expressed by vibration 1635.64 $cm^{-1}$ but Lewis acid sites not occurred. Absorption characteristics for Lewis acid sites on Al-pillared bentonite is lost due to heating at 500 °C due to the interactions that occur between the Lewis acid sites on the surface of bentonite with pyridine very weak is physiorption interaction[17].

Surface acidity was decreased due to the pillarization process from 1.656 mmol/g pyridine become 0.5436 mmol/g pyridine. It occured because of dehydration and dehydroxilation reaction take place in calcinations process. It caused decreased surface acidity especially Brønsted acid sites in Al-pillared bentonite.

**Chemical compositions of Al-pillared bentonite:** The chemical compositions of the raw bentonite and Al-pillared bentoniteas shown in Table-2. Table-2 showed that the composition of $SiO_2$ and $Al_2O_3$ increased the Al-pillared bentonite. Decrease of composition $Fe_2O_3$, MgO and CaO on Al-pillared bentonite due after the cation exchange process occurs in the space between the layers.

TABLE-2
COMPOSITION OF METAL OXIDE THE RAW BENTONITE AND Al-PILLARED BENTONITE

| Metal oxide (%) | Sample | |
|---|---|---|
| | Raw bentonite | Al-pillared bentonite |
| $SiO_2$ | 32.1950 | 35.9511 |
| $Al_2O_3$ | 0.1151 | 6.9576 |
| $Fe_2O_3$ | 8.5053 | 4.8322 |
| MgO | 0.0085 | 0.0070 |
| CaO | 6.3269 | 0.8861 |

**Catalytic activity in esterification reaction:** Catalytic activity of Al-pillared bentonite in esterification reaction studied *via* the esterification reaction of acetic acid with ethanol to produce ethyl acetate. The percentage of ethyl acetate product produced through esterification reaction using a catalyst raw bentonite and Al-pillared bentonit are shown in Table-3.

TABLE-3
PERCENTAGE OF CONVERSION OF ACETIC ACID AND ETHYL ACETATE PRODUCTS

| Catalyst | Conversion of acetic acid (%) | Ethyl acetate (%) |
|---|---|---|
| Raw bentonite | 46.79 | 8.61 |
| Al-pillared bentonite | 67.01 | 16.74 |

Table-3 shows the percentage of Al-pillared bentonite produce ethyl acetate is formed higher than raw bentonite. This occurs because the pillarization process improve the physico-chemical properties like specific surface area and total pore volume. Specific surface area and total pore volume is expected that considerable more adsorbed reactant and possibility of a bigger reaction. Increased interaction of the catalyst and the reactans indicated the formation of products and increase the activity of catalyst. Although the surface acidity measurements showed the surface acidity of raw bentonite is higher than Al-pillared bentonite. Based on this, it can be concluded that the catalytic activity of bentonite is not only influenced by the acidity of the surface but also influenced by the surface properties of the bentonite material such as surface area and total pore volume.

Percentage of ethyl acetate produced by Al-pillared bentonite is not too high. This is due to the existence of water molecules resulting from the dilution of acetic acid used. In the presence of an esterification reaction the water molecules present in the reaction system resulted in two negative effects: (1) rapid reaction between the catalyst and the water causes the deactivation of the catalyst so that the catalytic activity decreases (2) The presence of water causes the ester hydrolysis reaction so that equilibrium shifted to the left (reactants). This resulted in the reduction of the amount of ester produced in esterification reactions[18,19].

The process of deactivation of the catalyst caused by the presence of water molecules of solvation of protons ($H^+$) is strong on the catalyst by water molecules resulting in lower acid strength of the catalytic protons. As a result, the concentration of protonated acetic acid ($CH_3COOH_2^+$) is reduced. In the esterification reaction, the reaction rate is determined by the attack nucleophilic alcohol to acetic acid protonated molecules so that if the concentration of acetic acid protonated molecules ($CH_3COOH_2^+$) is low then it inhibit the formation of ethyl acetate (ester)[1].

**Effect of length of alcohol's carbons chain:** To compare the alcohol employed in the reaction might have, three different alcohols have been used : methanol, ethanol and *n*-propanol. The operational conditions were similar for all experience. The effect that the length of the alcohols carbon chain has on the conversion of acetic acid show in Table-4.

TABLE-4
CONVERSION OF ACETIC ACID AND PERCENTAGE OF ESTER PRODUCTS WITH DIFFERENT ALCOHOLS

| Alcohols groups | Conversion of acetic acid (%) | Esters (%) |
|---|---|---|
| Methanol | 48.42 | 9.55 |
| Ethanol | 57.89 | 1.65 |
| *n*-Propanol | 64.20 | 0.96 |

Based on the data in Table-4 the percentage of ester produced using methanol solvent is higher than ethanol and *n*-propanol although the conversion of aceticacid and *n*-propanol higher than methanol and ethanol. This suggests that the longer the carbon chain, the greater the size of the alcohol molecules are formed ester percentage is getting smaller.

In general, a catalyst metal particles dispersed on a porous carrier, the active site is more dominant on the surface so that the reactant molecules must diffuse inside the pore to meet with the catalytic active sites and adsorbed. The small size of the alcohol molecules in the pores will move faster than the alcohol molecules are larger in size as a result a growing number of small alcohol molecules to be adsorbed on the catalyst surface so that the chances of interaction with acetic acid on the surface of the catalyst to produce esters greater. The percentage of ester produced is not proportional to the conversion of ethyl acetate. This is likely because most of the acetic acid adsorbed on the catalyst surface is too strong so it is difficult to react with the alcohol molecules to form ester products.

## Conclusion

The present study showed that significant improvement on physico-chemical characteristics of the bentonite samples was obtained by a pillarization process using metal oxide aluminium. Such process also provided improvements on catalytic activities in esterification reaction. It was observed from catalytic activity test that pillared bentonite aluminium demonstrated higher activity in esterifcation reaction relative to the raw bentonite. It was demonstrated that catalytic activity pillared bentonite aluminium was not only affected by surface acidity but also affected by surface physico-chemical character *i.e*. specific surface area and total pore volume. The length of the alcohols carbon chain has effect on the conversion of acetic acid and percentage of ester products.

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