

12-20-2016

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Recommended Citation

Chidi, Obi and Peter, Okoye Ifedi (2016) "The Use of Eco-Friendly Catalyst in the Production of Ester," *Makara Journal of Science*: Vol. 20 : Iss. 4 , Article 7.

DOI: 10.7454/mss.v20i4.6708

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Cover Page Footnote

The authors wish to thank the Cardiff Catalysis Institute, School of Chemistry, University of Cardiff, UK 350 and E.M. Unit, Universiti Sains Malaysia, for providing the laboratory facilities for the structural characterization of Al-pillared and natural bentonite. The helpful suggestions provided by Prof. G.J. Hutchings are gratefully acknowledged.

The Use of Eco-Friendly Catalyst in the Production of Ester

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Received August 5, 2016 | Accepted November 27, 2016

Abstract

This study utilized an eco-friendly heterogeneous catalyst in the synthesis of ester via esterification of ethanol and acetic acid under refluxing conditions. The amount of acetic acid converted was determined by titrimetric method. Aluminum pillared material was produced from natural clay by ion exchange and calcined at 473 K. Powdered X-Ray diffraction (PXRD), Fourier Transform Infra-Red (FT-IR) and BET gas sorption analysis were employed to characterize the pillared material. The result revealed that significant improvement on physicochemical characteristics of the natural clay occurred as a result of pillaring. The results also revealed that the conversion of acetic acid was dependent on the catalyst/feed ratio of 2:2:1. The maximum conversion of acetic acid of 95.79% was obtained at the reaction temperature of 363 K and 150 minutes. The pillared clay material is more active in the conversion of acetic acid than the natural bentonite clay. This study illustrated that pillared bentonite clay is an eco-friendly solid catalyst for use in the production of chemical precursors for several industrial products.

Abstrak

Penggunaan Katalis Ramah Lingkungan dalam Produksi Ester. Penelitian ini memanfaatkan katalis heterogen ramah lingkungan pada sintesis ester melalui esterifikasi etanol dan asam asetat dalam keadaan refluks. Jumlah asam asetat yang terkonversi ditentukan dengan metode titrimetri. Material berpilar aluminium dibuat dari tanah lempung alam melalui proses tukar kation dan dikalsinasi pada 473 K. Difraksi sinar-X untuk bubuk (PXRD), Fourier Transform Infra-Red (FT-IR) dan analisis sorpsi gas BET digunakan untuk karakterisasi material berpilar tersebut. Hasil menunjukkan adanya penyempurnaan yang signifikan pada karakter psiko-kimia dari tanah lempung alami sebagai hasil dari pilarisasi. Hasil menunjukkan pula bahwa konversi asam asetat bergantung pada rasio katalis/umpan, sebedari 2:2:1. Konversi maksimum asam asetat sebesar 95.79% diperoleh pada suhu reaksi 363 K dan 150 menit. Material tanah lempung terpilar terlihat lebih aktif pada konversi asam asetat dibandingkan dengan tanah lempung bentonit alami. Penelitian ini member gambaran tentang bentonit terpilar sebagai katalis padat ramah lingkungan untuk digunakan dalam pembuatan prekursor bahan kimia untuk berbagai produk industri.

Keywords: Al-Pillaring, clay catalyst, esterification, heterogeneous reaction, % conversion of acetic acid

Introduction

Esterification is a chemical process widely employed in the organic process industry to produce esters. It is an extremely slow and reversible process in the absence of catalysts at room temperature, thus it is often carried out in the homogenous phase in the presence of mineral acid catalysts such as sulphuric acid, hydrochloric acid, etc. However, due to inherent problems like corrosion, rate reduction, loss of catalyst, separation and environmental problems associated with the use of mineral acids, efforts are being made to develop environmental friendly heterogeneous catalysts for the synthesis of esters [1-2].

The flavors and aromas associated with fruits and flowers are due to the presence of active compounds of esters, which accounts for the high demand for esters in wine and allied industries.

In recent times, many research workers have carried out investigations on esterification of carboxylic acids with alcohols in the presence of solid acid catalysts [3-4]. Studies have shown that the conversion of carboxylic acid with alcohol to esters using different types of catalysts are influenced by the nature of the catalyst, type of solvent used and operation conditions [5-6]. Esterification pretreatment can be used in the production

of biodiesel which is an alternative to fossil fuel from the laboratory to the industry [7]. This is essential both from the academic and industrial standpoints.

Pillared clays are considered to be interesting two-dimensional zeolite-like, shape selective molecular sieves and have been widely used as catalysts or catalyst support in the petroleum and petrochemical industries, due to their pore size and enhanced acid sites properties [8]. The principle behind clay pillaring originates from the insertion of voluminous or oligomeric inorganic metal hydroxycations between the layers of clays in order to keep them apart. On calcination, the metal hydroxycations are decomposed into oxide pillars, which create interlayer and interpillar spaces [9-10]. These authors discovered that thermally stable inorganic moieties can be intercalated between the individual clay lamellar sheets. The intercalated materials were transformed into metal oxide acting as pillars through calcination. The pillared materials were demonstrated to have an increased interlamellar distance, an increased pore volume and were accessible by molecules within a specific size range [11]. The surface of the pillars posses both Lewis and Bronsted acid sites [12]. The Bronsted acidity is attributed to the separation of the clay interlayer by pillaring and consequent surface exposure of the sylanol groups. The need to utilize our natural resources and make our environment cleaner and safer has led to this study.

In this work, the synthesis of ester via esterification of ethanol and acetic acid under refluxing conditions has been investigated in the presence of eco-friendly catalyst.

Materials and Method

Natural clay sample was collected from the open clay deposit in Ezinachi, Okigwe Local Government Area, Imo state, Nigeria. The clay sample was washed and dried under sunshine for two days. Aluminum pillared material was produced by ion exchange and calcined at 473 K [13]. Elemental analysis of the natural and pillared clay samples was performed using Atomic Absorption/Emission Spectrophotometer. Nitrogen adsorption-desorption isotherm was determined at 77 K in an Autosorb-I (Quantachrome). Samples of 0.2302 g were out-gassed at 453 K under vacuum. The specific surface area (SSA) was determined based on BET [14] model. The specific total pore volume was determined from the adsorption at the relative pressure of 0.95, converted to liquid volume assuming a nitrogen density of 0.808g/mL. The micro pore size distribution was analyzed based on the methods proposed according to Ahmad *et al.* [15] and Michal and Mietek, [16]. Powder X-ray diffraction (PXRD) patterns were recorded using a Philips APD 1700 instrument, with quartz plate CuK α radiation of wavelength 1.5406 Å [17]. The framework vibration of the natural and pillared samples was studied in the range of 400-4000 cm⁻¹ using Infrared spectroscopy (FTIR) [13]. Esterification process was

carried out homogeneously using a three-necked round bottom glass flask of 250 ml capacity fitted with a reflux condenser and mercury in glass thermometer to monitor the temperature as described by Bhimashankar *et al.* [18]. The mole ratios of acetic acid to ethanol used for this experiment at 363 K for 150 mins was 1:1, 2:1, 3:1, 4:1 and catalyst weight of 2.0 g. The concentration of acetic acid consumed during the reaction was calculated according to the following formula below [18].

$$\text{Concentration of acetic acid (M)} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{V_{\text{CH}_3\text{COOH}}} \quad (1)$$

Where C_{NaOH} = concentration of sodium hydroxide in molarity, V_{NaOH} = volume of sodium hydroxide used in titration in dm³ and $V_{\text{CH}_3\text{COOH}}$ = volume of reaction mixture sample titrated measured in dm³.

However, the percentage conversion of acetic acid was equally calculated by the formula below [19]:

$$\text{Concentration of acetic acid (\%)} = \frac{[A_c]_o - [A_c]}{[A_c]_o} \times 100 \quad (2)$$

Where $[A_c]_o$ = initial concentration of acetic acid (M) and $[A_c]$ = measured concentration of acetic acid at time of sampling (M).

Results and Discussion

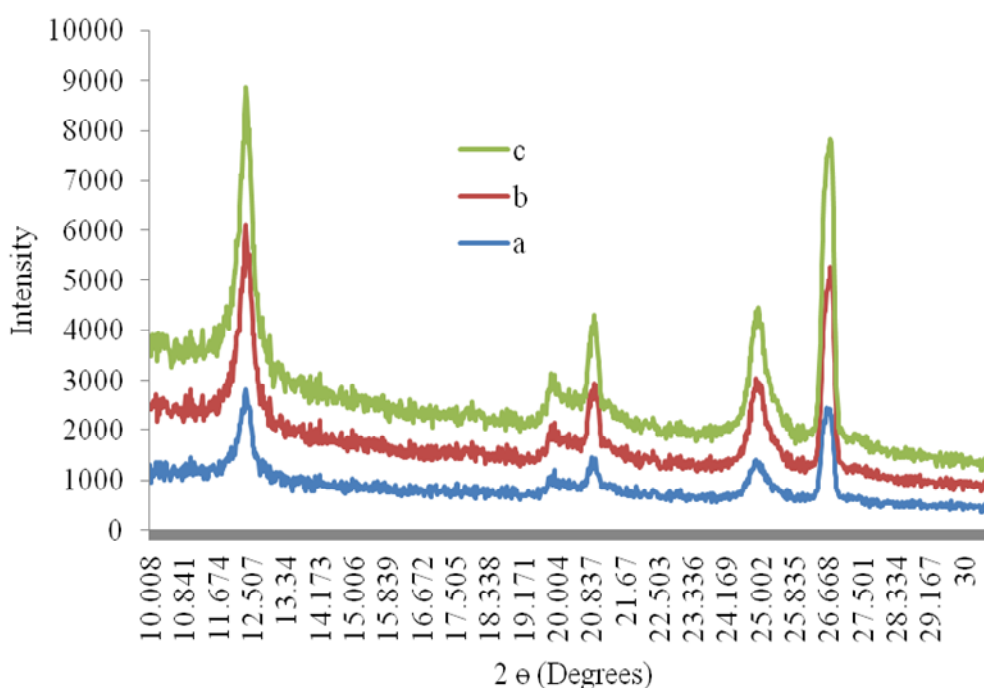
Catalyst characterization and esterification process.

The chemical composition of natural and pillared bentonite clay as presented in Table 1 indicated that the natural bentonite contained silica, alumina, magnesia, iron oxide and sodium oxide as major constituents while traces of calcium and potassium oxides exist as impurities. On pillaring, the aluminum content increased while other metals decreased significantly, due to ion exchange and washing several times with water. The decrease in the amount of exchangeable metal cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Fe³⁺) upon pillaring is clearly seen because, apart from washing, the entrance of Al-Pillar replaces exchangeable cations.

The PXRD patterns of the natural, intercalated and pillared bentonite clay catalyst is presented in Figure 1. The PXRD pattern of the natural bentonite showed lower intensity than the corresponding intercalated and pillared clay. This could be as a result of ion exchange between the aluminum ion and the native ions on the clay's interlayer. The main reflection at d_{001} showed a slight shift toward lower angle (2θ), resulting in a slight decrease in basal spacing due to the conversion of Al³⁺ to the oxide form.

Table1. Physicochemical Compositions of the Natural and Al-pillared and Bentonite Clay

| Metal oxides (% Wt) | Natural bentonite | Al-Pillared bentonite |
|--------------------------------|-------------------|-----------------------|
| SiO ₂ | 74.12 | 71.20 |
| Al ₂ O ₃ | 0.50 | 16.99 |
| Fe ₂ O ₃ | 7.88 | 3.42 |
| CaO | 0.02 | 0.01 |
| MgO | 0.23 | 0.15 |
| Na ₂ O | 0.04 | 0.02 |
| TiO ₂ | Nil | Nil |
| K ₂ O | 0.11 | 0.01 |

**Figure 1. PXRD Pattern of (a) Natural, (b) Al-Intercalated and (c) Al-Pillared Clay**

Mid-infrared spectroscopy is a very important tool for investigating structural changes in pillared clay frameworks. The region of interest for obtaining structural information is within the region of 1400-400 cm^{-1} which is characteristic of metal bonded silica [20-21]. The FTIR spectra of the parent (natural) bentonite, aluminum intercalated and pillared bentonite clay is presented in Figure 2. The spectra of the natural bentonite showed an intense peak at around 1400 cm^{-1} that is due to bending vibrations of water. The Si-O coordination bands at 1160, 1120 and 1110 cm^{-1} are due to the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheet.

A medium to strong peak at 1050 cm^{-1} is attributed to asymmetric stretching vibration of SiO₂ tetrahedra. These peaks are noted to decrease in intensity due to the process of dehydration and dehydroxylation involved during pillaring. The observed bands at 550 cm^{-1} and 450 cm^{-1} are due to Al-O-Si groups of the octahedral and Si-O-Si bending vibrations, respectively. The intensities

of the peaks were slightly reduced in the pillared bentonite in comparison with the intercalated and natural bentonite clay. This could be as a result of the large substitution of the clay interlayer cation by Al³⁺ ion [22]. A small peak in the hydroxyl bending region at 850 cm^{-1} assigned to isolated Al-O vibration becomes significant for Al-pillared sample but was completely absent in the spectrum of natural bentonite, which clearly suggest that the octahedral cations (Fe, Mg) are being replaced by aluminum. The process of pillaring substitutes a large amount of interlayer cations that generally existed in hydrated forms and thus decreased the hydroxyl ion contents. It has been shown that pillared clays have low amount of adsorbed/coordinated water due to dehydroxylation [20]. Bands around 1000 cm^{-1} are due to symmetric vibrations of Al³⁺ tetrahedral. The doublet at 800 and 780 cm^{-1} indicates the presence of quartz impurity in the sample in accordance with the recent report by Madejova *et al.* [23].

The pillaring also affected the textural properties of the materials. The total and micro pore surface areas, pore volume and average pore diameter of the material are listed in Table 2. In the case of pillared sample, the total surface area (ca. $49.86 \text{ m}^2\text{g}^{-1}$), the micro-pore surface area (ca. $3.3 \text{ m}^2\text{g}^{-1}$), the total pore volume ($0.013 \text{ cm}^3\text{g}^{-1}$) and the average pore diameter are significantly higher than that of the natural bentonite due to the presence of micro-pores created by aluminum pillar in the interlayer regions. The average pore diameter is within the range typical of smectite clays [19].

Effect of catalyst loading on conversion of acetic acid. The performance of the catalysts, as illustrated by Figure 3, clearly indicated that the conversion of acetic acid increases with increase in catalyst weight. Thus, maximum conversion of acetic acid of 95.79% was obtained at catalyst loading of 2.0g and acetic acid to ethanol mole ratio of 2:1 at a temperature of 363 K. The result further showed that pillaring with aluminum leads to a significant increase in acetic acid conversion compared to natural clay catalyst. In addition, the reactant molecules were thought to achieve greater

access to the clay inter-layers, since the PXRD pattern showed that there was an increase in basal spacing and pore size during pillaring [24]. It was found that small amount of acetic acid was converted at zero catalyst loading which was in line with the work reported by Jinesh *et al.* [25]. This was explained by considering the fact that acetic acid is a protonic acid which functions as a homogenous catalyst having active H^+ ions for the reaction. Lux *et al.* [26] subsequently provided evidence for the occurrence of autocatalysis via molecular acetic acid to account for the product obtained in the absence of the solid acid catalyst.

Effect of mole ratio on conversion of acetic acid. The effect of mole ratio of the reactants on conversion of acetic acid studied over Al-pillared clay catalyst is represented in Figure 4. Initially, the conversion of acetic acid increased with increase in the mole ratios of the reactants from 1:1 to 2:1, but decreased with further increase in the mole ratio. This can be attributed to the occupation of the catalyst active sites by the acid molecules and the availability of alcohol molecules for esterification [27].

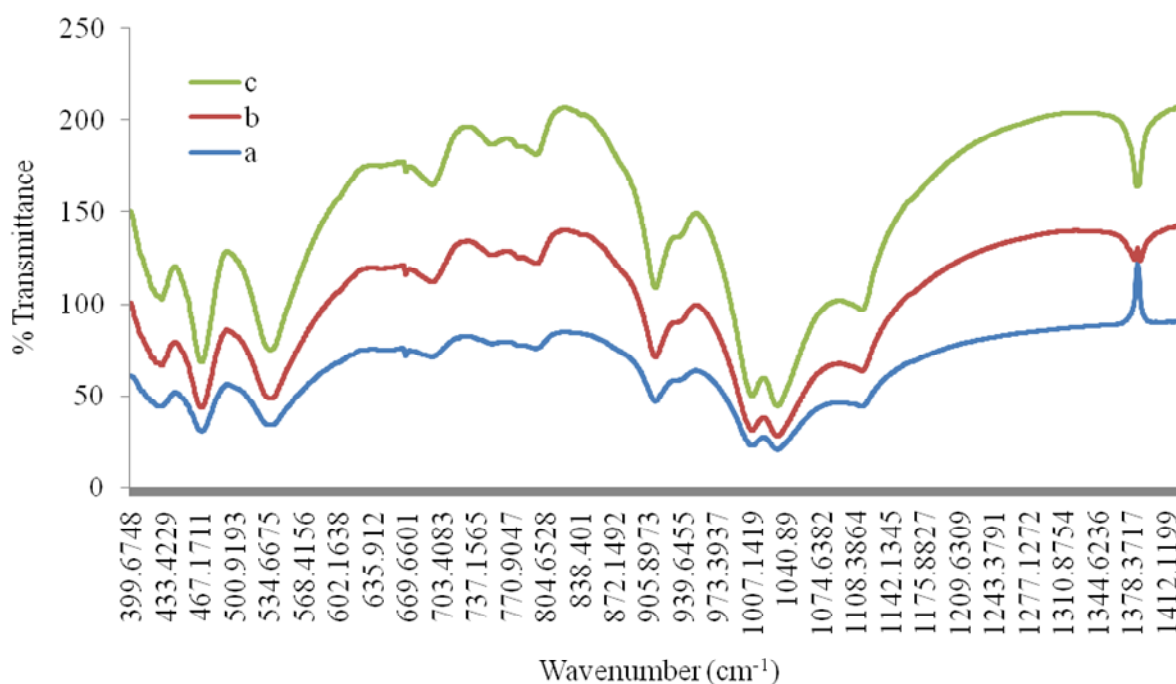


Figure 2. FTIR Spectra of (a) Natural, (b) Al-Intercalated and (c) Al-Pillared Bentonite Clay

Table 2. Total Surface and Micro Pore Areas, Micro Pore Volume and average Diameter of Natural and Al-pillared Bentonite

| Sample | Total Surface Area (m^2/g) | Micro-pore Volume (cm^3/g) | Micro-pore Area (m^2/g) | Total Pore Volume (cm^3/g) | Average Pore Diameter (\AA) |
|-----------------------|--|--|---|--|--|
| Natural bentonite | 30 | 0.001 | 2.60 | 0.001 | 14.8 |
| Al-Pillared bentonite | 49.86 | 0.0012 | 3.30 | 0.013 | 16.2 |

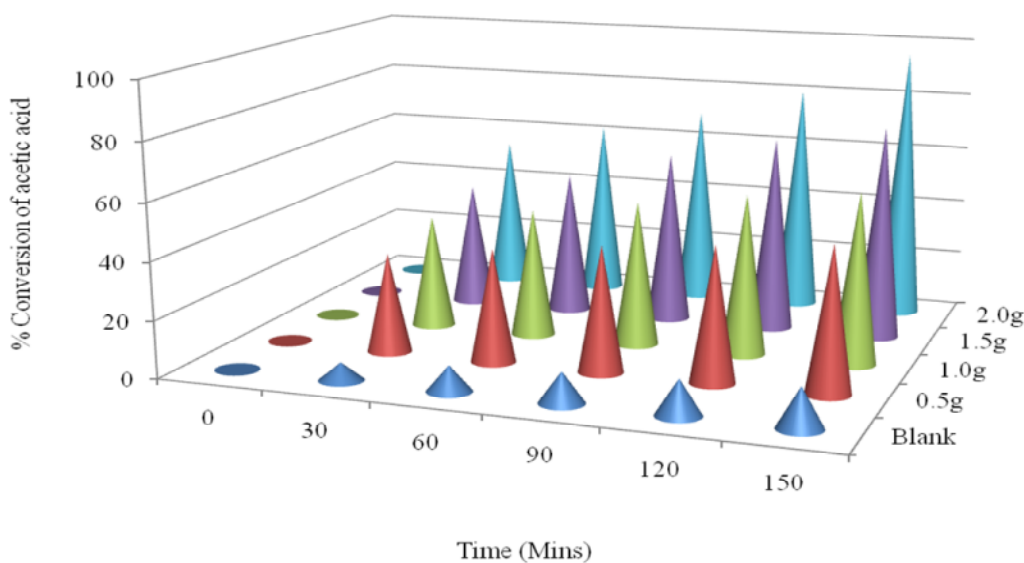


Figure 3. Effect of Catalyst Loading on Conversion of Acetic Acid on Al-pillared Clay Catalyst

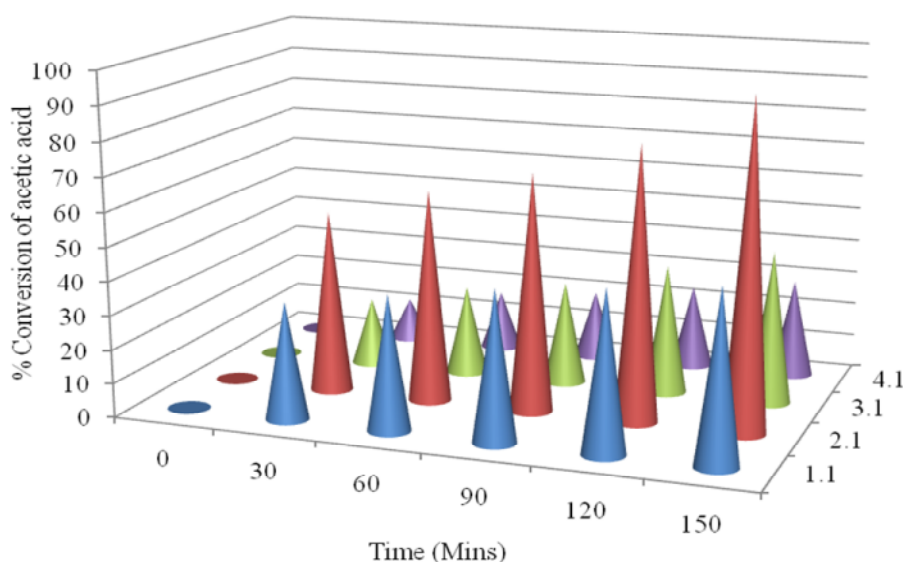


Figure 4. Effect of Mole Ratio on Conversion of Acetic Acid for Al-pillared Clay Catalyst

Conclusions

The PXRD investigation indicated an increase in basal spacing in the clay due to the insertion of alumina pillar, while the FTIR spectra revealed that the structure of the clay material did not collapse following calcination. The catalytic results showed that the conversion of acetic acid increased with increased catalyst loading and reaction time. The highest conversion of acetic acid (95.79%) was obtained at an acid to alcohol mole ratio of 2:1. This work has demonstrated that Al-pillared clay has potential for esterification and trans-esterification of carboxylic acids.

Acknowledgments

The authors wish to thank the Cardiff Catalysis Institute, School of Chemistry, University of Cardiff, UK 350 and E.M. Unit, Universiti Sains Malaysia, for providing the laboratory facilities for the structural characterization of Al-pillared and natural bentonite. The helpful suggestions provided by Prof. G.J. Hutchings are gratefully acknowledged.

Competing Interests

The authors declare that no competing interests exist.

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