The Preparation and Application of Environmentally Benign Titanium Pillared Clay Catalyst for Esterification of Ethanol and Acetic Acid

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Authors’ contributions

This work was carried out in collaboration between all authors. OIP designed the study and read the first draft of the manuscript. OC and MAI performed the experiment, calculations and all the analyses of the study. OC managed the literature searches and the final corrections on the manuscript. All authors read and approved the final manuscript.

ABSTRACT

Aims: The study is aimed to develop an indigenous heterogeneous based catalyst and evaluate kinetic mechanism for the synthesis of ethyl acetate by esterification of acetic acid and ethanol.

Study Design: Batch reactor system.

Place and Duration of Study: Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers State, Nigeria. The study was carried out between February to August, 2011.

Methodology: A sample of the natural clay 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. Titanium pillared bentonite was produced by modification of natural bentonite clay using titanium pillaring solution at 500°C. X-Ray diffraction (XRD), Fourier Transform Infra-Red (FTIR) and BET gas sorption analysis were employed to characterize the pillared material. Esterification reactions were carried out in a batch mode 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. Heating

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and stirring was achieved using a magnetic hot plate with a stirrer. Pre-determined amount of acetic acid (for 1:1, 2:1, 3:1, 4:1 acid: alcohol mole ratio) and the clay catalyst were charged into the reactor and heated to 90 ±0.5ºC. After the desired temperature has been reached, a known amount of ethanol preheated separately using heating mantle was added into the reactor. About 2 ml of the reaction mixture was taken immediately using Pasteur pipette and titrated against 0.1 M NaOH solution using phenolphthalein indicator. All the experimental runs were designed by varying the amount of the catalyst, the acid to alcohol mole ratios, and the reaction period to obtain various kinetic parameters while keeping the temperature constant for all the runs.

**Results:** The result revealed that significant improvement on physicochemical characteristics of the bentonite samples occurred as a result of pillaring. The results obtained revealed that the conversion of acetic acid was dependent on the catalyst weight, reaction time and mole ratio. The maximum conversion of acetic acid was obtained for mole ratio (acid: alcohol) of 2:1 with optimum catalyst weight of 2.0g at a reaction temperature of 368K and 90 minutes time on-stream. The pillared clay material was shown to be more active in the conversion of acetic acid than the unpillared counterparts. Kinetics studies revealed that the esterification reaction is second-order and follows the single step Eley-Rideal reaction mechanism.

**Conclusion:** The esterification results showed that the conversion of acetic acid increased as a result of pillaring than the zero and unpillared catalyst. The mechanism involves a nucleophilic attack between adsorbed acetic acid and unadsorbed or competitively adsorbed ethanol to give ethyl-acetate and water. This research has demonstrated that titanium pillared clay has potential for esterification and trans-esterification of carboxylic acids.

**Keywords:** Esterification; pillarization; catalyst; kinetics; homogenous reaction.

### 1. INTRODUCTION

The chemical industries worldwide are facing the challenges of stringent environmental regulations amidst severe market competitiveness. There is a growing demand for chemical processes that are clean, energy efficient, intrinsically safe and responsive to market needs. In order to meet these objectives, chemical industries are driving towards more environmentally friendly processes that meet requirements such as generation of nearly zero waste chemicals, less energy consumption, use of less hazardous chemicals, reusable materials etc (James and Duncan, 2002).

Catalysts are by far a major player in the chemical industry. It is often used to increase the rate of reaction in chemical processes. Homogeneous catalysts such as hydrofluoric acid (HF), sulphuric acid (H₂SO₄), hydrochloric acid (HCl) etc, are the main catalysts used in catalysis. Since green approach in chemical processes was conceived, there has been a strong interest in the use of more environmentally friendly solid acid catalysts as a replacement to homogeneous catalysts (James and Duncan, 2002). Although these mineral acid catalysts are very effective, it produces highly corrosive media with chemically reactive substances. Purification can be both difficult and hazardous when used to catalyse a chemical process (Toor et al., 2010).
On the other hand, the solid acid counterparts are easier to handle, reusable, purification is simpler and cheaper and more environmentally friendly and the general operation of a large chemical process is safer. Because of these desirable properties of heterogeneous catalysts, it has become increasingly attractive as an alternative catalyst.

Many heterogeneous catalysts such as clay minerals, pillared clay minerals, exchange resins, zeolites, amorphous silica-alumina, etc have been reported to be active in esterification reactions (Igbokwe et al., 2004, 2008; Zheng and Zeng, 1998; Nijhuis et al., 2002; Alime et al., 2007). Esterification reactions occurring without catalyst is extremely slow, since the rate is dependent on the autotrolysis of the acetic acid (Mehdi, 2010). Consequently, esterification is enhanced by the presence of acid catalyst, which acts as donor to the acid. Both homogenous and heterogeneous catalysts are used in the esterification reaction (Masakazu, 1994). Ethyl acetate is a colourless liquid and it has a characteristic smell. It is used primarily as a solvent and is used in many applications. It is used extensively as a solvent for high-resolution printing inks and laminating adhesives. It is used to dissolve the pigments for nail varnishes, and is responsible for the solvent-effect of some nail varnish remover (Loudon, 2002). There are large deposits of bentonite clay minerals across the parts of Nigeria. Clays have been used as acidic catalysts in petroleum cracking and several other organic reactions. Natural untreated clays possess a very low ability to catalyse reactions in either polar or non-polar media. However, the structural properties of these materials can be modified by various methods in order to produce catalysts with high acidity, surface area, porosity and thermal stability. To enhance performance, research is now focused on the synthesis of pillared clays (PILCs), which posses’ larger two-dimensional pores (Fatimah et al., 2011). Pillaring is achieved by the insertion of voluminous inorganic metal hydroxycation between layers of the clay in order to keep them apart. On thermal treatment, the metal hydroxyations are transformed into pillars which are responsible for the acidity (Miguel et al., 2009; Okoye and Obi, 2011). The surface of the pillars posses both Lewis and Bronsted acid sites (Salerno et al., 2001; Issaadi et al., 2006). 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.

Therefore, in this work, preparation, characterization and kinetic evaluation of indigenous pillared clay based active catalyst from Nigerian bentonite for esterification reactions are reported. This is a strategy to add value to our local content.

2. MATERIALS AND METHODS

2.1 Clay Source and Sampling

A sample of the natural clay 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.

2.2 Catalyst Preparation

The pillaring agents were prepared following the method described by Lin et al. (1993). Titanium chloride (TiCl₄) from Aldrich was mixed with twice the volume of ethanol, and stirred in a solution of glycerol. The total mixture was added drop wise to a calculated amount of clay in 250ml of deionised water and allowed to equilibrate under stirring for
4 hours at room temperature. The titanium intercalated clay material was filtered and dried overnight in an oven at 110°C. The intercalated Ti-clay was calcined at 500°C for 4 hours in air to give the Ti-pillared clay (Ti-PILC).

2.3 Catalyst Characterization

An elemental analysis of the natural and pillared clay samples was performed using Atomic Absorption/Emission Spectrophotometer. Nitrogen adsorption–desorption isotherm were determined at –196°C in an Autosorb – I (Quan-Tachnome). Samples of 0.2302g were out gassed at 180°C under vacuum. The specific surface area (SSA) was determined based on BET (Brunauer et al., 1938) 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 by Horvath and Kawazoe, (1983) and by Saito and Foley (1991). Powder X-ray diffraction (PXRD) patterns were recorded using a Philips APD 1700 instrument, with quartz plate CuKα radiation of wavelength 1.5406 Å (Ckowksi and Joshi, 2007). The vibrational framework of the pillared sample was studied using Infrared spectroscopy (FTIR). Scanning electron microscope (LEO SUPRA 50VP-FIELD EMISSION SEM, Carl Zeiss, Germany) was used to observe the surface morphology of the clay samples.

2.4 Catalytic Activity Studies

Esterification reactions were carried out in a batch mode using a three-necked round bottom glass flask of 250ml capacity fitted with a reflux condenser and mercury in glass thermometer to monitor the temperature (Fig. 1).

Fig. 1. Schematic representation of the batch reactor used for this study

Heating and stirring was achieved using a magnetic hot plate with a stirrer. Pre-determined amount of acetic acid (for 1:1, 2:1, 3:1, 4:1 acid: alcohol mole ratio) and the clay catalyst were charged into the reactor and heated to 90±0.5°C. After the desired temperature has been reached, a known amount of ethanol preheated separately using heating mantle was added into the reactor. About 2 ml of the reaction mixture was taken immediately using
Pasteur pipette and titrated against 0.1 M NaOH solution using phenolphthalein indicator. All the experimental runs were designed by varying the amount of the catalyst, the acid to alcohol mole ratios, and the reaction period to obtain various kinetic parameters while keeping the temperature constant for all the runs. The concentration of acetic acid consumed during the reaction was calculated by the following formula (Bhimashankar et al., 2010).

$$\text{Concentration of acetic acid (M)} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}} \text{(dm}^3\text{)}}{V_{\text{CH}_3\text{COOH}} \text{(dm}^3\text{)}}$$

With:

- $C_{\text{NaOH}}$: Concentration of sodium hydroxide in molarity
- $V_{\text{NaOH}}$: Volume of sodium hydroxide used in titration in $\text{dm}^3$
- $V_{\text{CH}_3\text{COOH}}$: Volume of reaction mixture sample titrated measured in $\text{dm}^3$

The percentage conversion of acetic acid was equally calculated by the formula below (Fatimah et al., 2011):

$$\text{Conversion of acetic acid (%) } = \frac{[\text{Ac}]_0 - [\text{Ac}]}{[\text{Ac}]_0} \times 100$$

With:

- $[\text{Ac}]_0$: initial concentration of acetic acid (M)
- $[\text{Ac}]$: measured concentration of acetic acid at time of sampling (M)

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The XRD patterns of the natural, Ti-Intercalated and Ti-Pillared bentonites in the $2\theta = 30^\circ$ range is represented in Fig. 2.

![PXRD patterns](image)

**Fig. 2.** PXRD pattern of (A) Natural, (B) Ti-Intercalated and (C) Ti-Pillared bentonite clay
Fig. 2 shows the XRD patterns of the natural, intercalated and pillared bentonite clay. The XRD pattern of the natural bentonite showed higher intensity than the corresponding intercalated and pillared clay. This could be as a result of ion exchange between the titanium ion and the native ions on the clay interlayer. The d-spacing for the titanium-intercalated bentonite is 15.0 Å. The d-spacing for the titanium-pillared (Ti-PILBe) bentonite calcined at 500°C is 22.0 Å. The main reflection at d₀₀₁ showed a slight shift toward lower angle (2θ) indicating an increase in d-spacing as a result of pillaring. These results reveal that the pillared clay samples have good ordered layers and that the insertion of titania pillar, was responsible for an increase in the clay basal spacing. Similar result was reported by Yamanaka and Makita (1995) with TiO₂ pillared montmorillonite.

Mid-infrared spectroscopy is a very important tool for investigating structural changes in pillared clay frameworks. The region of interest for determining structural composition is the frequency region between 1400 - 400 cm⁻¹ which is characteristic of metal –oxygen bonded framework (Fig. 3) (Gill and Gandia, 2000). Peaks at around 1400 cm⁻¹ are due to bending vibrations of water. The introduction of titania on the bentonite by pillaring broadens the bands due to the presence of more –OH groups of the pillar. The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The process of pillaring substitutes a large amount of interlayer cations that generally exist in hydrated forms and thus decreases the intensity of –OH peaks. It has been shown that pillared clays have low amount of adsorbed/co-ordinated water due to the non-swelling nature. Thus, pillaring reduces the intensity of the bands around 1400 cm⁻¹. The intensity of the peak was reduced in the pillared bentonite much more than the intercalated and natural bentonites respectively. This could be as a result of the isomorphous substitution of the native ions in the clay interlayer by titanium ion (Lin et al., 1993). The very intense band centred at 1300 cm⁻¹ is due to asymmetric stretching vibrations of SiO₄ tetrahedra. Bands consisting of peaks of medium intensity at 450 - 550 cm⁻¹ are due to bending vibrations of Si-O.

Fig. 3. FTIR spectra of (A) Natural, (B) Ti-Intercalated and (C) Ti-Pillared bentonite clay
The results of the surface area measurement also show the pore evolution after pillaring. The BET and micro pore surface areas, pore volume and average pore diameter of the material are listed in Table 1. The BET specific surface of the pillared material increased as a result of pillaring. The porosity of the pillared material is higher than the unpillared, although an expanded material is obtained. This is confirmed by the low total pore volume of the sample.

Table 1. BET surface and micro pore areas, micro pore volume and average diameter of natural and Ti-pillared bentonite

| Sample          | BET surface area (m²/g) | Micro pore volume (cm³/g) | Micro pore area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (Å) |
|----------------|-------------------------|---------------------------|------------------------|---------------------------|--------------------------|
| Natural bentonite | 30                      | 0.001                     | 2.7                    | 0.001                     | 14.8                     |
| Ti-Pillared bentonite | 68                      | 0.009                     | 18.6                   | 0.016                     | 16.2                     |

3.2 Effect of Catalyst Loading on Conversion of Acetic Acid

The result in Fig. 4a clearly indicated that conversion of acetic acid increases as catalyst loading was increased, which was attributable to an increase in total number of available catalyst active sites. Thus, maximum conversion of acetic acid was obtained at catalyst loading of 2.0 g and acetic acid to ethanol mole ratio of 2:1 at a temperature of 368 K. This observation is consistent with the proposed reaction mechanism given below.

Fig. 4b also showed that pillaring with titanium results to a significant increase in acetic acid conversion compared to unpillared clay catalyst. This observed trend may be due to an increase in acid strength, both Bronsted and Lewis acidity as a result of pillaring. In addition, the reactant molecules were thought to achieve greater access to the clay interlayers, since the XRD pattern showed that there was an increase in basal spacing and pore size during pillaring. It was found that small amount of acetic acid was converted at zero catalyst loading which is in line with the work recently reported by Joyce and Nagaraju (2006). 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. Po¨pken et al. (2000) 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 (depicted in Fig. 3a).

3.3 Effect of mole ratio on conversion of acetic acid

The effect of mole ratio of the reactants on conversion of acetic acid studied over Ti-pillared clay catalyst is represented in Fig. 5. 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. The acid molecules are chemisorbed on the active sites of the catalyst to form carbonium ions in accordance with Eley–Rideal mechanism. The attack by the alcohol on these positively charged ions to form ester is least effective at low reactant concentration, but becomes significant at higher reactant concentration leading to an increase in conversion. Increasing the mole ratio of acetic acid to alcohol further from 2:1 to 4:1, leads to a decrease in
conversion of acetic acid, probably due to increase in the hindrance of nucleophilic attack as the excess acid shields the alcohol molecules from attacking the protonated acyl carbon atoms of the acid, in accordance with Eley-Rideal reaction mechanism (Robert, 2008).

Fig. 4a. The effect of catalyst loading on the conversion of acetic acid: (368 K, 90 minutes Time-on-line and acid: alcohol mole ratio of 2:1)

Fig. 4b. The effect of different type of catalyst on the conversion of acetic acid: (368 K, 90 minutes Time-on-line and acid: alcohol mole ratio of 2:1)
3.4 Kinetics of Esterification of Acetic Acid and Ethanol

The reaction kinetics for the esterification of acetic acid and ethanol using Ti-pillared clay catalyst was studied using the integral method of analysis of rate data to determine the order of the esterification reaction. Rate data were obtained at 368K for different acid to alcohol mole ratio and by varying the amount of the catalysts. In order to determine the order of the esterification reaction, equations 2 and 3 given below were used to plot a graph of \( \ln [\text{CH}_3\text{COOH}]_t \) against time \( t \) for first order and \( 1/[\text{CH}_3\text{COOH}]_t \) against time \( t \) for second order models.

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \\
\ln [\text{CH}_3\text{COOH}]_t & = -kt[\text{CH}_3\text{COOH}]_0 \quad \text{(1st order equation)} \quad \text{......... 1} \\
\frac{1}{[\text{CH}_3\text{COOH}]_t} & = kt + \frac{1}{[\text{CH}_3\text{COOH}]_0} \quad \text{(2nd order equation)} \quad \text{......... 2}
\end{align*}
\]

Where \([\text{CH}_3\text{COOH}]_0\) and \([\text{CH}_3\text{COOH}]_t\) are the concentrations of acetic acid at zero time and at any time \( t \). Figs. 6 and 7 depict the plots of first order and second order reactions respectively at different catalyst loading while Figs. 8 and 9 depict the plots of first order and second order reactions respectively at various acid to alcohol mole ratio. From these plots, it was observed that the correlation coefficient of the second order reaction gave a better fit than the correlation coefficient of first order reaction, hence it can be concluded that the esterification of acetic acid and ethanol in excess acetic acid using Ti-pillared clays as catalyst follows the second order reaction. The rate constants and the correlation coefficients

Fig. 5. Effect of acid: alcohol mole ratio on conversion of acetic acid: (368 K, 90 minutes Time-on-line and catalyst weight of 2.0g)
were obtained from the slopes of the linear regression of these plots and are given in Tabs. 2 and 3.

Fig. 6. Plot of ln[A] against time at different catalyst loading and fixed acid: alcohol ratio = 2.1

Fig. 7. Plot of 1/[A] against time at various catalyst loading (acid : alcohol = 2.1)
Fig. 8. Plot of In [A] against time at various acid to alcohol mole ratio: (catalyst weight of 2.0g)

Fig. 9. Plot of 1/ [A] against time at various acid to alcohol mole ratio: (catalyst weight of 2.0g)
Table 2. The kinetic data for the formation of ethyl acetate at different catalyst loading: (368 K, 90 minutes Time-on-line and acid: alcohol mole ratio of 2:1)

| Catalyst (g) | Second order |  | First order |  |
|--------------|--------------|-----------------|--------------|-----------------|
|              | Rate constant (k) | Correlation coefficient | Rate constant (k) | Correlation coefficient |
|              | (dm³ mol⁻¹ s⁻¹) |                     | (dm³ mol⁻¹ s⁻¹) |                     |
| 0.5          | 0.0017        | 0.973             | 0.0023        | 0.957             |
| 1.0          | 0.0025        | 0.967             | 0.0027        | 0.941             |
| 1.5          | 0.0031        | 0.967             | 0.0036        | 0.934             |
| 2.0          | 0.0034        | 0.950             | 0.0034        | 0.907             |

Table 3. The kinetic data for the formation of ethyl acetate for various acid: alcohol mole ratio (2.0 g catalyst, 368 K and 90 minutes Time-on-stream)

| Acid:alcohol mole ratio | Second order |  | First order |  |
|-------------------------|--------------|-----------------|--------------|-----------------|
|                         | Rate constant (k) | Correlation coefficient | Rate constant (k) | Correlation coefficient |
|                         | (dm³ mol⁻¹ s⁻¹) |                     | (dm³ mol⁻¹ s⁻¹) |                     |
| 1:1                     | 0.0052        | 0.930             | 0.0024        | 0.889             |
| 2:1                     | 0.0034        | 0.951             | 0.0032        | 0.907             |
| 3:1                     | 0.0012        | 0.830             | 0.0026        | 0.795             |
| 4:1                     | 0.0006        | 0.751             | 0.0019        | 0.724             |

3.5 Reaction Mechanism

A plot of 1/r₀ against 1/Cₐ,O in Fig. 11 shows that the initial reaction rate increases linearly with acid concentration, thus suggesting that the esterification of acetic acid with ethanol followed Eley-Rideal mechanism. The first step in the reaction mechanism involves the adsorption of the acetic acid on a catalyst active site. This is followed by a nucleophilic attack of an alcohol molecule on the adsorbed acetic acid to form ethyl acetate and water.

![Reaction mechanism diagram]

Fig. 10. Plausible reaction mechanism for the esterification of acetic acid and ethanol over Ti-Pillared clay
4. CONCLUSION

In this study, titanium pillared bentonite was successfully prepared and characterized by XRD and FTIR. The XRD spectra indicated an increase in basal spacing in the clay by insertion of titania pillars, and the FTIR spectra revealed changes in the framework structures as a result of pillaring. This phenomenon is explained in terms of the large substitution of the native ions in the clay interlayer by titanium ion. The esterification results showed that the conversion of acetic acid increased with increasing catalyst loading and reaction time. It was also found that the highest conversion of acetic acid was obtained at acid to alcohol mole ratio of 2:1. The kinetic data also showed that the reaction follows the Eley-Rideal (ER) mechanism, which involves a nucleophilic attack between adsorbed acetic acid and unadsorbed or competitively adsorbed ethanol to give ethyl-acetate and water. The order of the esterification reaction was found to be second-order and the surface reaction was considered the rate limiting step of the esterification reaction. This research has demonstrated that titanium pillared clay has potential for esterification and transesterification of carboxylic acids.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.
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