Research Journal of Engineering Sciences ISSN 2278 – 9472
Vol. **2(2),** 7-10, February **(2013)** *Res. J. Engineering Sci.*

Nigerian Clay as a Catalyst for Esterification of Propan-1-ol with Propanoic Acid

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Available online at: www.isca.in
Received 6th January 2013, revised 17th January 2013, accepted 20th January 2013

Abstract

The esterification of propan-1-ol with propanoic acid using Nigerian clays as catalysts was carried out in a batch reactor. Catalysts samples were produced from thermally activated clays obtained from Suleja and Shabu, Nigeria respectively. The effect of mole ratio and catalyst concentration on the conversion was studied. The thermally activated Suleja clay gave a highest conversion of 59 % at catalyst concentration (3%) and mole ratio (acid: alcohol) of 1:2, at a reaction temperature of 70 ^{O}C, While thermally activated Shabu gave the highest conversion of 55% at same process variable conditions. The increase in alcohol to acid mole ratios resulted to decrease in percentage conversion. While increase in catalyst concentration led to increase in percentage conversion.

Keywords: shabu-clay, suleja-clay, catalyst, esterification, propanoic acid, propan-1-ol.

Introduction

Clay catalysts have received considerable attention in different organic syntheses due to their environmental compatibility, low cost, high selectivity, thermal stability and reusability. Contemporary studies have investigated clay's absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification as well as its ability to catalyzed different organic reactions[1,2]. This includes; alkylation, condensation, dimerization, isomerization and esterification reactions amongst others[3]. Catalytic technologies play a key role in the economic development and growth of the chemicals industry and contribute to around 20% of world GNP. A major emerging and challenging area of heterogeneous catalysis is that of environmental pollution control, with tightening legislation on the release of waste and toxic emissions having serious implications for the chemical industry[4]. While heterogeneously catalyzed processes are widely used within the petrochemical industry, many fine and specialty chemicals manufacturers rely on homogeneously catalyzed liquid-phase reactions. Many of these processes were developed at the turn of the century, and focused on product yield, disregarding the environmental impact of inorganic waste and toxic by-products formed during the reaction[5]. A wide range of liquid-phase industrial reactions rely on the use of inorganic or minerals acids. While many of these processes are catalytic, some require (e.g., acylation using aluminum trichloride) stoichiometric amounts of acid. Final isolation of the product necessitates aqueous quenching and neutralization steps to remove the acid, resulting in enormous quantities of hazardous waste, with the cost of disposal of this waste often outweighing the value of the product. Tightening legislation on the emission of hazardous pollutants is driving the industry toward the implementation of innovative "clean technology" including the use of alternative heterogeneously catalyzed processes[4]. Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product usually in the presence of a mineral acid as catalyst (e.g. sulphuric acid). Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odour. This leads to their extensive use in the fragrance and flavour industry as constituent in the productions of perfumes, cosmetics, paints, nail varnishes and artificial flavours for foods. Esterification is among the simplest and most often performed organic transformations[6,7]. This study aimed to investigate and compare esterification of propan-1-ol with propanoic acid using catalyst produced from Nigerian clay. This was based on the effect of process variables such as acid to alcohol mole ratio, catalyst concentration and temperature on the percentage conversion as well as reaction rate.

Material and Methods

Experimental Procedure: The clay samples used were collected from Suleja and Shabu, Nigeria was pretreated by sun dried, crushed and sieved. Samples with particle size in the range of 500 to 750 microns, and subsequently clay samples were thermally activated in a furnace (Ogawa Sieki, Japan) at 400^{o}C (673K) for four hours and ready for use in the esterification reaction. Propanoic acid and propan-1-ol (analytical grade) were used without further purification. A batch reactor consisting of a three-necked flat bottom flask of 250cm^3 capacity, fitted with a reflux condenser and a sampling device. Stirring was achieved using a high speed magnetic

stirrer combined with a regulated heating mantle. All the runs were carried out at high stirring speed to overcome the mass transfer film diffusional resistance. The calculated amount of propan-1-ol was put into the three-necked flask and heated to the appropriate temperature for the run. An appropriate amount of propanoic acid (for the given mole ratio of alcohol to acid) was added to the determined quantity of catalyst in a separate flask and heated slightly above the required temperature. The mixture of acid and catalyst was added to the alcohol. Samples were drawn at time intervals and titrated against standard solution of sodium hydroxide using phenolphthalein indicator. All the runs were carried out in a similar manner by using the following process variables: catalyst concentration (% mass) 0, 1, 2, and 3; mole ratio of alcohol from 1:1 to 4:1 and temperatures 50^{o}C, 60^{o}C, and 70^{o}C, respectively. Two different catalyst types, Suleja clay and Shabu clay, were used in these runs alternatively. The effects of different catalysts, catalyst loading and temperature on the reaction kinetics were evaluated.

Results and Discussion

Effect of catalyst concentration and mole ratio on the reaction: The effect of catalyst concentration of 1 %, 2 % and 3 % on the reaction kinetics at 70^{O}C is shown in figure 2 for thermally activated Suleja clay catalyst and figure 6 for thermally activated Shabu clay catalyst, respectively. It was observed that the degree of conversion increased with the catalyst concentration. On the other hand, the conversion was also seen to decrease as the mole ratio of alcohol to acid increased (figures 3 and 7). This was attributed to the increase of the alcohol molecules on the active sites of the catalyst hindering the adsorption of the acid and consequently showing the reaction as has also been noted in the literature. This indicates that the adsorption of the carboxylic on the catalyst in this reaction is necessary and is hindered in the presence of an excess of alcohol. Thus, the adsorption of the acid is hindered by the competitively adsorbing alcohol, a behavior which can be explained using both the Langmuir – Hinshelwood and – Rideal kinetic models [8].

Effect of clay catalyst type (Suleja and Shabu clays): Figures 4 and 8 showed that Suleja clay catalyst generally gave higher conversions than Shabu clay catalyst. This was attributed to the differences in composition of the two clays. This can be accounted for by the higher Bronsted and Lewis surface acidity in Suleja Kaolinite[3]. In addition, Suleja clay is characterized by high porosity owing to its imperfect crystal formation and thermal activation of the clay with a higher moisture content resulted in dehydration and subsequent creation of more active sites for the adsorption of the reacting species.

Effect of the reaction temperature: Reactions were carried out at 50, 60 and 70^{O}C in preliminary runs in this work to determine the effect of temperature on conversion using two clay catalyst samples at 3% loading. It was seen that higher temperatures gave the greater conversions for both clay catalysts, with Suleja clay having a higher percentage conversion than Shabu clay. The maximum conversions were obtained at 343K. Thus, an increased in temperature generally favoured the forward reaction as described in the literature[9,10,11].

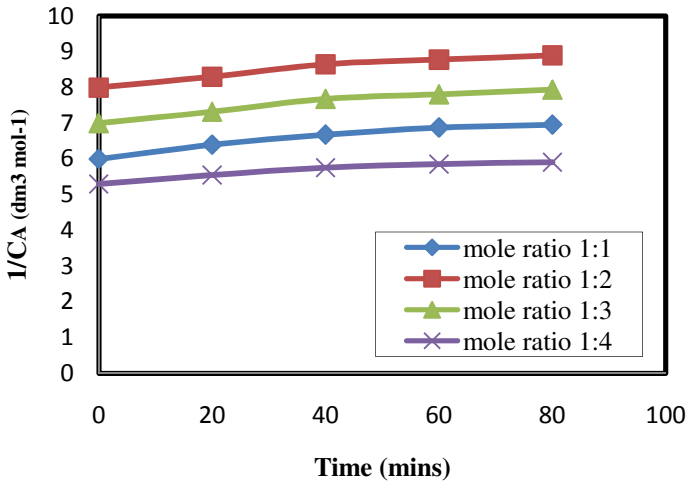

Figure-1
Pseudo first order for mole ratio using thermally activated Suleja clay

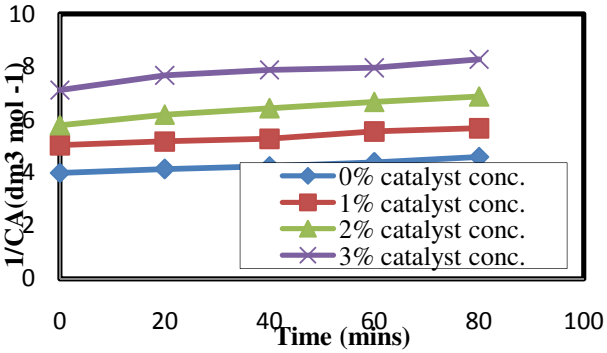

Figure-2
Pseudo first order for effect catalyst concentration using thermally activated Suleja clay

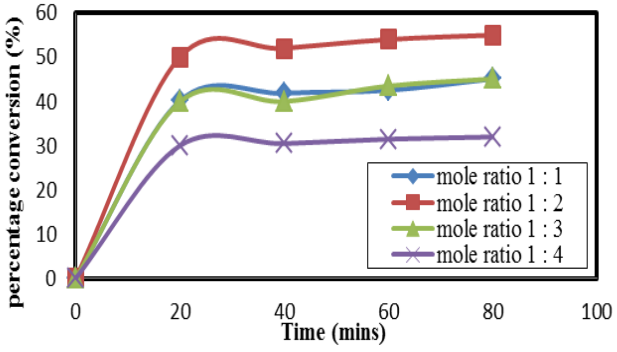

Figure-3
Effect of mole ratio on % conversion of propanoic acid using thermally activated Suleja clay

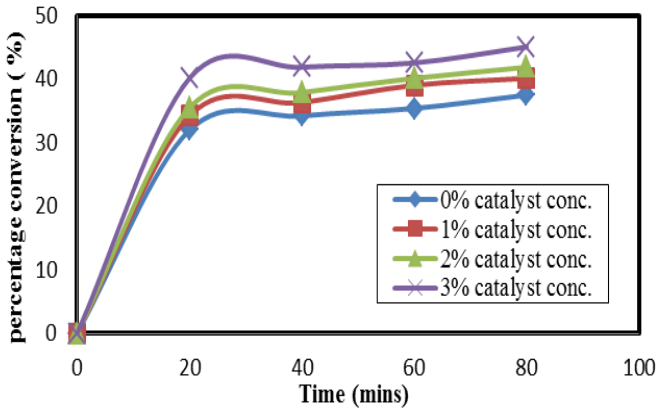

Figure-4
Effect of catalyst concentration on % conversion of propanoic acid using thermally activated Suleja clay

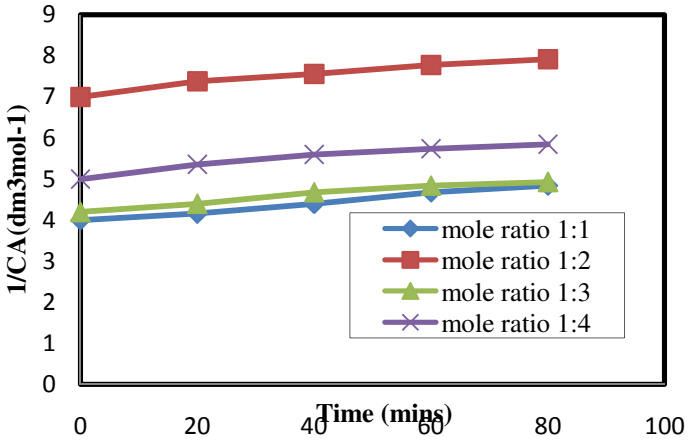

Figure-5
Pseudo first order for mole ratio using thermally activated Shabu clay

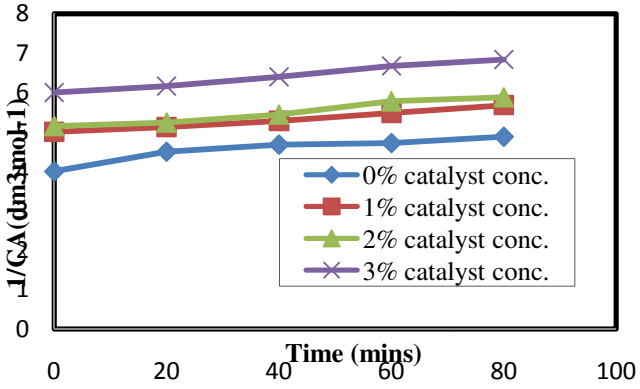

Figure-6
Pseudo first order for effect of catalyst concentration using thermally activated Shabu clay

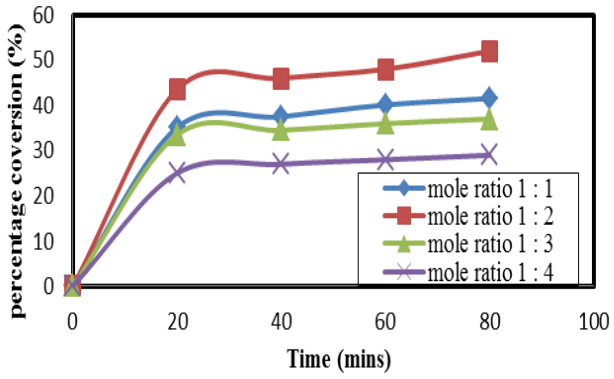

Figure-7
Effect of mole ratio on % conversion of propanoic acid using thermally activated Shabu clay

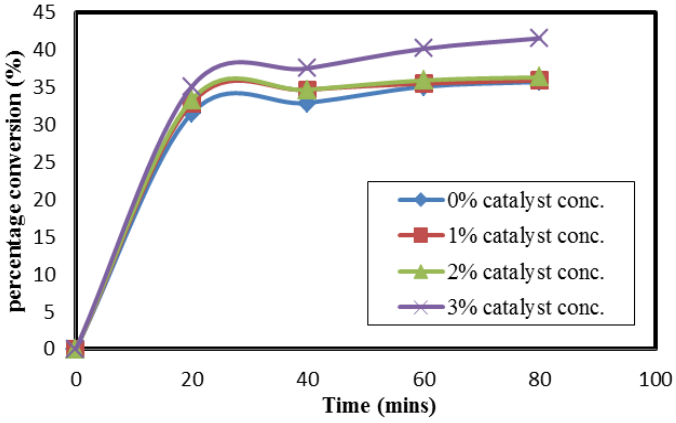

Figure-8
Effect of catalyst concentration on % conversion of propanoic acid using thermally activated Shabu clay

Table-1
Kinetic Parameters from LHHW Model

Parameters	Value
Ar	2E05 mol/gmin
Ar	2E05 mol/gmin
Eo	42.55Kj/mol
K_A	0.22
K_B	2.09
Kc	0.27
K_D	2.19

Rate of reaction data: The rate of reaction for the esterification reaction was obtained using integral method of analysis. This was done as a function of the concentration of the participating components, which corresponds to the rate law, which is proportional to time[12]. The rate parameters were obtained at 343K for different mole ratios of acid to alcohol and different clay catalyst concentrations. It can be seen from figures 1-2 and 5-6, that the plots of C^{-1}_A versus time (t) in minutes showed a second order reaction for the esterification reactions, with both Suleja and Shabu clay at different mole ratios of acid and the

alcohol. The specific rate constant for the esterification with Suleja and Shabu clays was determined to be approximately 0.011 dm^3 $mol^{-1}s^{-1}$. This is in agreement with Igbokwe *et al* [9]. This is an average of values calculated at various experimental kinetic data points, i.e. reactants concentrations at various reaction times[10,11].

Reaction mechanism and kinetic modeling: Applying the Lagmuir-Hinshelwood-Hougen-Watson (LHHW) model, and considering rate of adsorption of propanoic acid as the rate limiting step. Other assumptions employed are, i. adsorption occurs on vacant sites, ii. adsorbed molecules are immobile,(iii) vacant sites can accommodate one adsorbed species, and iv. heat of adsorption is constant for all sites. This means that there was no heat interaction between adjacent sites and these are also uniform. Therefore the rates of adsorption, surface reaction, desorption and also reactions are equal. Using the rate expression for LHHW model as shown in equation 1, the model parameters were estimated using least squares method. These parameters which are adsorption constant for propanoic acid, adsorption constant for propan-1-ol, adsorption constant for propylpropanoate, adsorption constant for water and adsorption constant for catalyst surface are shown in table-1.

$$Af\left(\frac{\mathrm{Eo}}{\mathrm{RT}}\right)\left(\mathrm{aAaB}-\left(\frac{\mathrm{Ar}}{\mathrm{Af}}\right)\mathrm{aCaD}\right)-\mathrm{rA}=(1+\mathrm{KBaB}+\mathrm{KDaD}) \quad (1)$$

Where: A_r and A_f = Pre-exponential factors for the forward and reverse reaction, E_o = Activation energy of the reaction, R = Gas constant, T = Reaction temperature, KB and KD = equilibrium constants for propan-1-ol and water.

The least square method was used to estimate the parameters obtained for esterification reaction at the temperature of 343K and catalyst concentration of 3%.These data are comparable with the previous findings[9,13,14].

Conclusion

The esterification of propan-1-ol using propanoic acid over thermally activated clay catalysts obtained from two Nigerian clays has been studied. The effect of catalyst concentration and mole ratios was revealed. Therefore, the percentage conversion was found to increase with catalyst concentration and decrease with increase in alcohol to acid mole ratio. The Suleja clay performed as a better catalyst than the Shabu clay. Comparison of the effect of the different catalysts showed that catalyst from clay generally gave higher conversions. Conclusively, the whole results obtained in this work conform to the previous researches carried out.

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