CATALYTIC ESTERIFICATION OF PROPANOIC ACID USING LOCAL KAOLINITE CLAY

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Abstract

The paper reports the study of catalytic esterification of propanoic acid using local kaolinite clay catalysts as performed in a batch reactor. The catalyst sample was produced from thermally activated local kaolinite clay obtained from Suleja, Nigeria. The effect of process variable such as mole ratio of (acid:alcohol), catalyst concentration and temperature on the conversion was studied. The highest conversion of 59 % was obtained from mole ratio (acid:alcohol) of 1:2 and 3 % catalyst concentration at a reaction temperature of 70 ^{O}C. The results of the effect of process variables showed that the degree of conversion increased with catalyst concentration and temperature. Whereas percentage conversion decreased with increase in alcohol to acid mole ratios. This work was undertaken so as to provide an environmentally acceptable and economically viable alternative catalytic medium in esterification reactions using locally available raw materials.

Keywords: kaolinite, catalyst, esterification, propanoic acid, propan-1-ol

Introduction

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 (Ababio, 1990). Esterification is amongst the simplest and most often performed organic transformations (Mark, 2002).Catalytic technologies play a key role in the economic development and growth of the chemicals industry and contribute to around 20 % of world GNP (Wilson and Clark, 2000). 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 (Wilson and Clark, 2000). 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 (Sheldon, 1997). 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 aluminium 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 (Wilson and Clark, 2000). Clay is a natural, earthy fine grained materials, which is powdery when dry, plastic when wet and stone –like when baked (Nwajagu and Oji, 1991; Nnuka and Apeh, 1991; Nwajagu and Aneke, 2001).There are three or four main groups of clay:kaolinite, montmorillonite-smectite,

illite and chlorite (Guggenheim and Martin,1995).Kaolin is a hydrated aluminium silicate crystalline mineral (kaolinite) formed over millions of years by hydrothermal decomposition of granite rocks. Kaolin is soft clay that is composed mainly of the mineral kaolinite (Deer *et al*; 1992).Because of the strong catalytic activity as Bronsted acid, activated kaolinite clay can be used in fine synthesis (Volzone *et al*; 2005).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 catalyze different organic reactions (Nagendrappa, 2002; Guggenheim and Martin, 1995). These includes; alkylation, condensation, dimerisation, isomerisation and esterification reactions amongst others (Konwar *et al,* 2007). Therefore the objective was to study 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.

Materials and Methods

The kaolinic clay samples obtained from Suleja, Nigeria was used to carry out this investigation. The sample was pretreated by sun drying, crushing and sieving. Samples with particle size in the range of 500 to 750 microns were selected for activation. The selected clay catalyst samples were thermally activated in a furnace at $400^{o}C$ (673K) for four hours and subsequently used for 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 was used for the reaction studies. Stirring was achieved using a high speed magnetic stirrer combined with a regulated heating mantle. All the runs were carried out at high stirrer speed to overcome the mass transfer film diffusional resistance. A 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 to acid from 1:1 to 4:1 and temperatures $50^{o}C$, $60^{o}C$, and $70^{o}C$, respectively. The effects of kaolinite clay catalyst loading and temperature on the reaction kinetics were studied.

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 4, for thermally activated Suleja clay catalyst. 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 (Figure 3). This behaviour could be attributed to the increase in the number of alcohol molecules on the active sites of the catalyst which hindered the adsorption of the acid which has also been noted in the literature (Missen *et al*, 1999). This further indicates that the adsorption of the carboxylic on the catalyst in this reaction is necessary and is hindered in the presence of an excess amount of alcohol molecules. 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 (Missen *et al*, 1999).

Effect of Kaolinite Clay Catalyst

Figure 4 show that Suleja kaolinite clay catalyst gave high conversions. This behaviour could be attributed to the mineral composition of the clay. This could also be due to the high Bronsted and Lewis surface acidity in Kaolinite clay (Volzone *et al*, 2005). In addition, kaolinite 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.
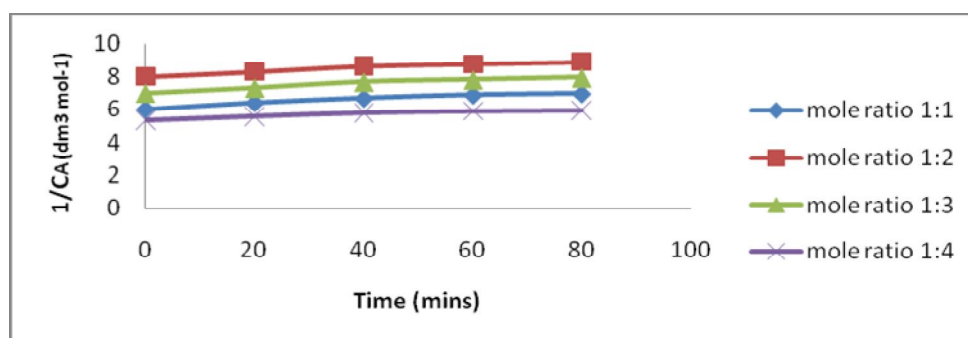

Figure 1:   Pseudo first order for mole ratio using thermally activated Suleja clay
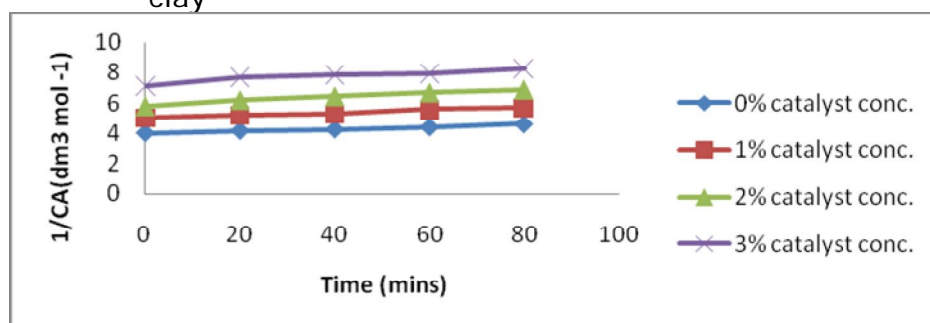

Figure 2:   Pseudo first order for effect catalyst concentration using thermally activated Suleja clay
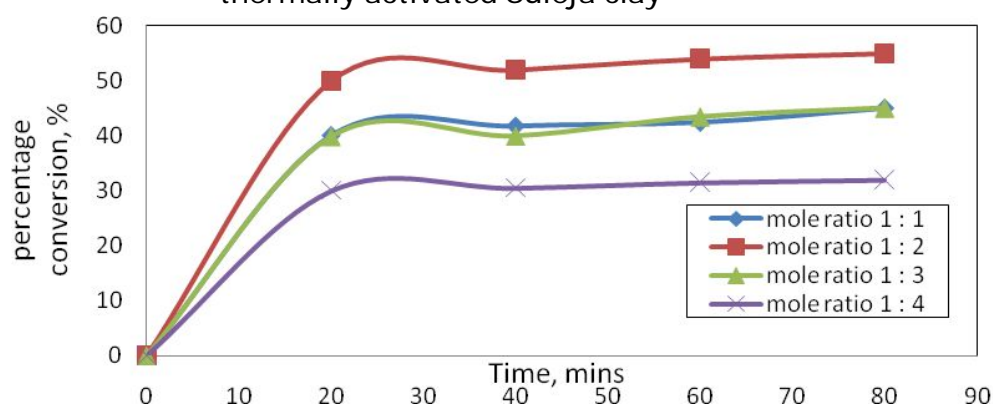

Figure 3:   Effect of mole ratio on % conversion of propanoic acid using thermally activated Suleja clay
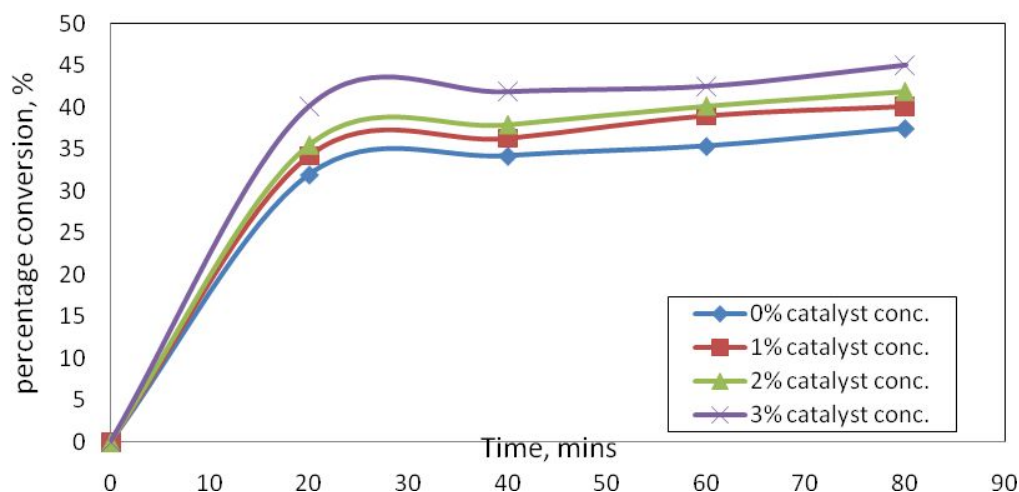
Figure 4: Effect of catalyst concentration on % conversion of propanoic acid using thermally activated Suleja clay

Effect of the reaction temperature

Reactions were carried out at 50, 60 and 70 ^{O}C to determine the effect of temperature on conversion rate using clay catalyst samples at 3 % loading. It was seen that higher temperatures gave the greater conversions for the clay catalyst. The maximum conversions were obtained at 343K. Thus, it shows that an increase in temperature generally favoured the forward reaction as confirmed in the literature (Igbokwe *et al*, 2008).The rate of esterification reaction was obtained using integral method of analysis. This was expressed as a function of the concentration of the participating components, which corresponds to the rate law, which is proportional to time (Falconer, 1998).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 and 2, that the plots of C^{-1}_A versus time (t) showed a second order reaction for the esterification reactions, with Suleja clay at different mole ratios of acid and the alcohol. The specific rate constant for the esterification with Suleja clay was determined to be 0.011dm^{3}mol^{-1}s^{-1} (Igbokwe *et al*, 2008). This is an average of values calculated at various experimental kinetic data points, i.e. reactants concentrations at various reaction times (Connors, 1990; Moore and Pearson, 1981).

Reaction mechanism

The rate expression for Lagmuir-Hinshelwood-Hougen-Watson (LHHW) model (Igbokwe *et al*, 2008) was used considering rate of adsorption of propanoic acid as the rate limiting step.Some 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.Therefore the rate of adsorption,surface reaction,desorption and also reaction are equal.

$A_f(E_o/RT)(a_A a_B - (A_r/A_f) a_C a_D) - r_{A} = (1 + K_B a_B + K_D a_D)$ (i)

Where : A_r & A_f = Pre-exponetial factors for the forward and reverse reaction, E_o = Activation energy of the reaction, R = Gas constant, T = Reaction temperature, K_B & K_D = equilibrium constants for propan-1-ol and water. Parameters obtained from the studies are, A_r & A_f = 2.00 x 10^5 mol g^{-1} min^{-1} , E_o= 42.55 KJ mol^{-1} ; $K_A a_A$ = 0.22 ; $K_B a_B$ = 2.09 ; $K_C a_C$ = 0.27 ; $K_D a_D$ = 2.19

Based on rate expression for (LHHW) model (Saha *et al*, 2005) as shown in equation (i).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 (Lee et al,2002; Saha et al;2005; Igbokwe et al,2008).

Conclusion

The kinetics of the esterification of propan-1-ol using propanoic acid over thermally activated clay catalysts obtained from Suleja 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. Conclusively, the locally kaolinite clay obtained from Suleja, Nigeria can serve as a catalyst in organic reactions.

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