

Synthesis of Amyl acetate using a Silica supported Heteropoly acid- A Kinetic Study

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ABSTRACT

There is an increase in the inclination of chemical industries towards new processes that should meet the requirements such as the generation of nearly zero waste chemicals, less energy and sufficient use of product chemicals in various applications. Esterification is one of the most widely employed reactions in the organic process industry. Most esterification reactions employ liquid acids as catalysts that cannot be recovered and also tend to corrode the reactors. This necessitates the use of heterogeneous eco-friendly catalysts. The present work focuses on the synthesis of isoamyl acetate using silica supported heteropoly acid. The catalyst was prepared by precipitation method. The performance of the catalyst was studied for the synthesis of isoamyl acetate at various reaction conditions such as mole ratio of reactants, temperature and catalyst loading. It was observed maximum acetic acid conversion of 90% was attained at 100°C, 1:3 and 3w/w% catalyst loading. Further, the kinetic studies were done and the activation energy was determined by the Arrhenius equation as 33.76 kJ/mol.

Keywords: Esterification, Heteropoly acid, Kinetics, Activation energy

1. Introduction

Esterification is one of the most widely employed reactions in the organic process industry. Most esterification reactions employ liquid acids as catalysts that cannot be recovered and also tend to corrode the reactors[1–4]. The heterogeneous catalysts provide various advantages such as easy separation, reusability and eco-friendly [3]. Quite a lot of solid catalysts employed in esterification reaction consist of ion exchange resins[1–8], sulphated zirconia[9-12], zeolites[13–16]. Catalysis by heteropoly acids (HPAs) and related compounds is a field of increasing importance. HPAs have several advantages as catalysts that make them economically and environmentally attractive [17-18]. Keggin structure heteropoly acids (HPAs) are extensively used as acid catalysts due to their extremely strong Brønsted acidity and structural properties [20]. From the literature, kinetic model development of various esterification reactions was reported with a homogenous catalyst[21]. Few attempts were made in developing the kinetic model for

esterification reaction with heterogeneous systems such as ion exchange resins[22-23]. In the present study, the phosphomolybdic was synthesized by the novel method of preparation which was not reported in the literature. Further, the phosphomolybdic acid was supported on silica. The efficacy of the catalyst was studied by performing experiments for the esterification of isoamyl alcohol with acetic acid at various reaction parameters. Additionally, the kinetics of the reaction were reported to facilitate the design of reactor which in turn helps for the continuous production of amyl acetate at a commercial scale.

1.1 Esterification of amyl alcohol

The reaction follows the normal esterification mechanism and gives the products amyl acetate and water.



2. Materials and Methods

2.1 Chemicals Used

IsoAmyl Alcohol, Sodium Hydroxide, Silicon dioxide and Phenolphthalein Indicator (Sd.fine Chemicals Ltd.) Ammonium Heptamolybdate, OrthoPhosphoric Acid, Hydrochloric Acid, Acetone, Acetic Acid (Merck Chemicals Ltd.).

2.2 Catalyst Preparation

Ammonium HeptaMolybdate and OrthoPhosphoric Acid of 1:12 are taken. Dissolved both chemicals in two beakers with an equal amount of water. Mixed them by pouring one to the other. Hydrochloric Acid was added dropwise to the solution mixture till the yellow precipitate stopped forming. The solution was filtered. Washed the precipitate using Acetone and left it to dry. The catalyst sample was dried in the oven at 110°C for 2 hours. The sample was calcined at 500°C for 4 hours. The yellow crystals of PhosphoMolybdic Acid (PMA) was Obtained. The silica support to the above synthesized phosphomolybdic acid was prepared by the impregnation method[85].

2.3 Experimental Procedure

The calculated amounts of isoamyl alcohol and acetic acid were taken in separate beakers for heating to the desired temperature. After the reactants attained the desired reaction temperature, they were mixed in the 3 – necked round bottom flask placed in an oil bath over a magnetic stirrer containing temperature control. The samples were withdrawn for specific time intervals, instantly centrifuged to take apart of the catalyst from the reaction mixture and brought down to below 5°C to cease the reaction. The sample drawn from the three neck round bottom flask was titrated against standardized 1N NaOH by using phenolphthalein as an indicator.

3. Results and Discussion

3.1 Effect of speed of agitation

The reaction was studied for four different speeds (400rpm, 500 rpm, 600rpm, and 700rpm) to study the effect of external mass transfer of reactants to the surface of the catalyst particle and also the significance of intra-particle diffusion. The experiments were carried out at 400rpm, 500 rpm, 600rpm, and 700rpm at 100°C, mole ratio (acid:alcohol)1:3,catalyst loading 3w/w%. It was observed from the figure 3.1 that the results obtained i.e. the conversion of acetic acid was nearly the same without much significant change, which means the speed of agitation does not have much significance on the rate of reaction and conversion. Hence all the other parameters are studied at 500 rpm.

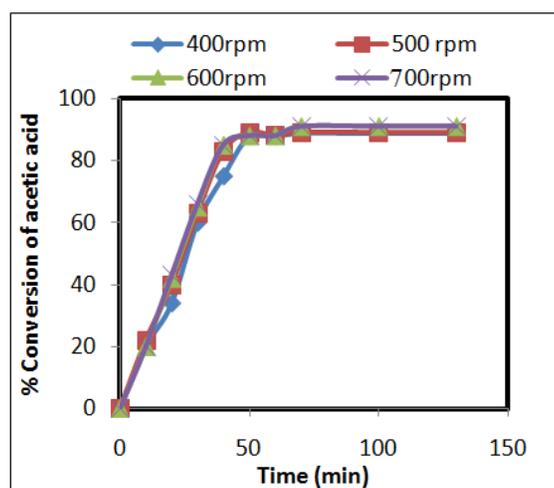


Figure 3.1: Effect of speed of agitation on acetic acid conversion

3.2 Effect of mole ratio of reactants

The studies were conducted at various mole ratios (acetic acid: amyl alcohol) 1:1, 1:3 and 1:5 at 100°C, 3w/w% catalyst loading. From figure 3.2 for a mole ratio of 1:1 the conversion of acetic acid obtained was 81.2% it shows that the catalyst exhibits better performance and for 1:3 the conversion of acid was 90% whereas at 1:5 the conversion of acetic acid was 91.5%. The rise in the mole ratio of acetic acid to amyl alcohol from 1:1 to 1:3 leads to an increase in the number of sites occupied by amyl alcohol molecules. With an increase in a molar ratio from 1:3 to 1:5 there is no significant increase in acetic acid concentration. Therefore the mole ratio of acetic acid to amyl alcohol 1:3 was used for all further investigations.

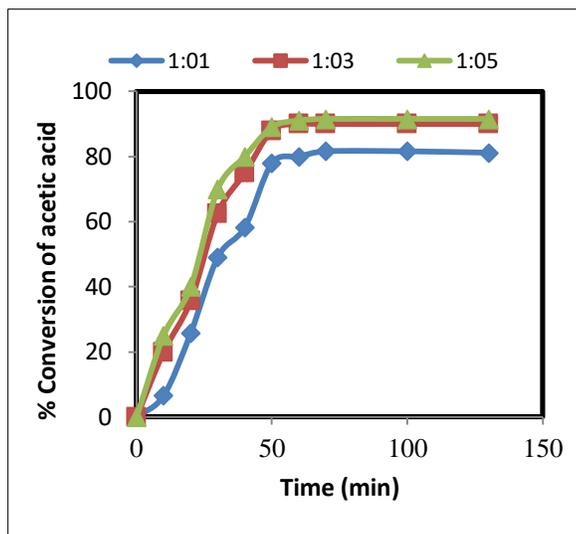


Figure 3.2 Influence of mole ratios on acetic acid conversion

3.3 Effect of Temperature

The temperature for the study was conducted at 70, 80, 90 and 100°C for a mole ratio of 1:3(acid: alcohol) and 3w/w% catalyst loading. From figure 3.3 it was observed that the conversion of acetic acid was enhanced from 63 % to 90% with rise in temperature from 70 to 100°C. The percentage increase in the conversion of acetic acid from 70°C to 80°C is 15% whereas from 80°C to 90°C was 8.0% and from 90°C to 100°C was 5%. The highest conversion of 90% was obtained at 100 °C. The previous work done by Yadav.et al. for esterification ethanol and maleic acid have reported the value of activation energy as 14.2 kcal/mol using Indion-170 catalyst[4].

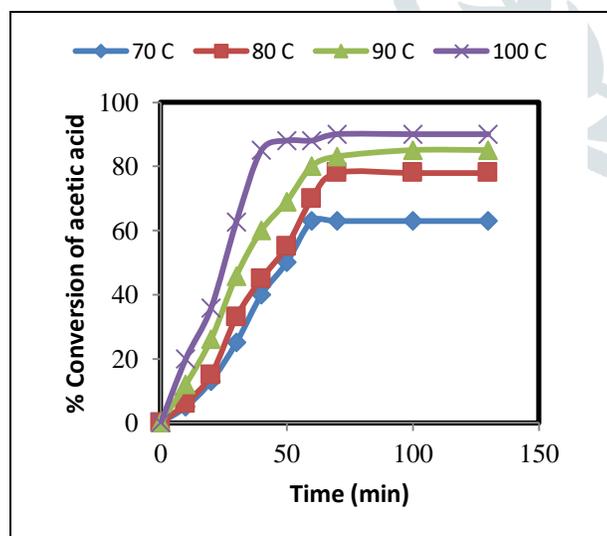


Figure 3.3: Influence of temperature on acetic acid conversion

3.4 Effect of Catalyst loading

The study was conducted at different catalyst loading varying from 1w/w% to 7w/w% at 100°C and 1:3 mole ratio (acid: alcohol). Figure 3.4 shows that the conversion of acid at 1w/w% of the catalyst was 83%, whereas with 3w/w % catalyst loading the conversion of acetic acid was 90% and at 5w/w% catalyst loading the conversion of acid was 92%. It was found that with an increase in catalyst loading the conversion of acid and rate of reaction also increased. There is no significant increase in acetic acid conversion with rise in catalyst loading from 3w/w% to 5w/w%. The reason may be beyond specific catalyst loading, the quantity of active sites was higher than that really required by the reactants.

The conversion of acetic acid at 7w/w% almost remained constant.

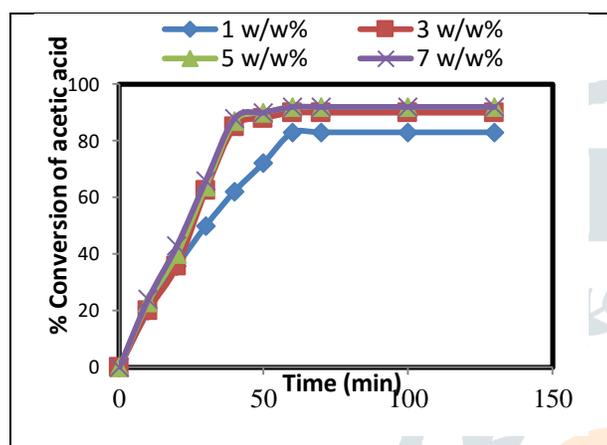
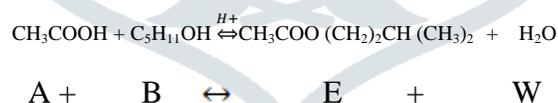


Figure 3.3: Influence of catalyst loading on acetic acid conversion

3.5 Kinetics of reaction

The esterification of amyl alcohol and acetic acid in the presence of acid catalyst is represented as follows:



The dual site mono functional Langmuir Hienshel Wood Hougen Watson model(LHHW) was developed, that is a reaction of two species adsorbed on different sites[25] .

In this study, the kinetic model was derived based on the following assumptions:

- The reaction was conducted at a stirring speed of 500 rpm such that the effect of mass transfer of the reactants is negligible.
- The concentration of one of the reactant is maintained excess in the experimentation such that the reaction proceeds in the forward direction. So that only the forward rate constant was considered in the kinetic model.

iii. The total reflux condition was maintained such that there is no loss of reactant during the reaction and the total amount of the reaction mixture is constant.

The steps or mechanism involved in the above reaction are

i) Adsorption of reactants

Adsorption of reactant acetic acid (A) on X, the vacant site is given by the expression as below:

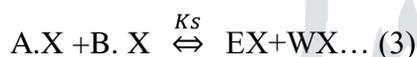


Adsorption of reactant isoamyl alcohol (B) on X, the vacant site is given by the expression as below:



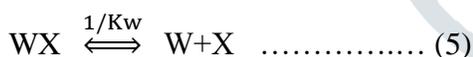
ii) Surface reaction

The surface reaction of AX and BX with the nearby active site, leading to the formation of products ester (EX) and water (WX) is represented by the equation:



iii) Desorption:

Desorption of Ester and Water from the active sites is represented by the equation:



The total concentration of monolayer i.e. the sites C_M is given as

$$C_M = C_A + C_B + C_E + C_W \dots\dots (6)$$

At equilibrium the rate of adsorption and desorption are equal, the concentration of vacant site can be given as

$$C_X = \frac{C_M}{1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W} \dots (7)$$

If surface reaction is the reaction controlling step, the rate of reaction of acetic acid (A) is given as

$$-r_A = -\frac{dC_A}{dt} = K_s C_{AX} C_{BX} - K_{s1} E_X W_X \dots (8)$$

$$-r_A = -\frac{dC_A}{dt} = \frac{k_2\{K_A K_B C_A C_B - \frac{K_E K_W C_E C_W}{K_2}\} C^2_M}{(1+K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \dots\dots\dots (9)$$

Since the mole ratio of alcohol is taken in excess to acetic acid, so the reaction favors the forward reaction and the reaction is at far from equilibrium, the above equation reduces to

$$-\frac{dC_A}{dt} = \frac{k_2 K_A K_B C_A C_B C^2_M}{(1+K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \dots (10)$$

The rate equation in terms of amount of catalyst is given as

$$-\frac{dC_A}{dt} = \frac{k_{R1} w K_B C_A C_B}{(1+K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \dots (11)$$

Let $k_{R1} w = k_2 K_A K_B C^2_M$, w the catalyst loading.

If the adsorption constants are low, the above equation reduces to

$$-\frac{dC_A}{dt} = C_A \frac{dX_A}{dt} = k_{R1} w (C_{A0} - C_{A0} X_A) (C_{B0} - C_{A0} X_A)$$

$$= k_{R1} w C_{A0} (1 - X_A) (\frac{C_{B0}}{C_{A0}} - X_A)$$

Integrating the equation on both sides we get the expression,

$$\ln \frac{(\frac{C_{B0}}{C_{A0}} - X_A)}{\frac{C_{B0}}{C_{A0}} ((1 - X_A))} = kt(C_{B0} - C_{A0})$$

Where $k = k_{R1} w$

Plot of $\ln \frac{(\frac{C_{B0}}{C_{A0}} - X_A)}{\frac{C_{B0}}{C_{A0}} ((1 - X_A))}$ vs t figure 3.5 gives a straight line passing through the origin as shown in the figure.

The slope of the line $k(C_{B0} - C_{A0})$ helps us to determine the rate constant at a particular temperature.

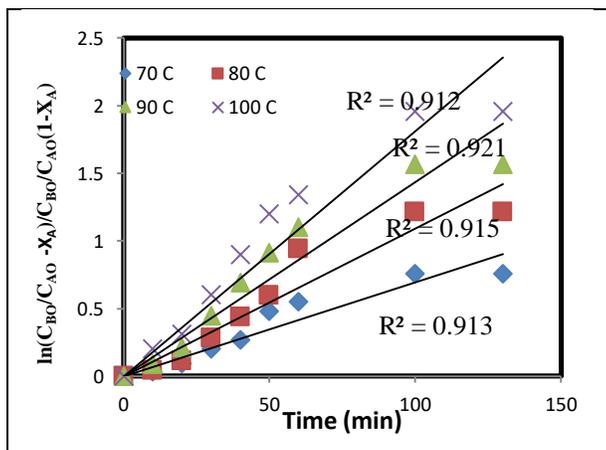


Figure 3.5: $\ln(C_{B0}/C_{A0} - X_A)/C_{B0}/C_{A0}(1-X_A)$ vs

Time

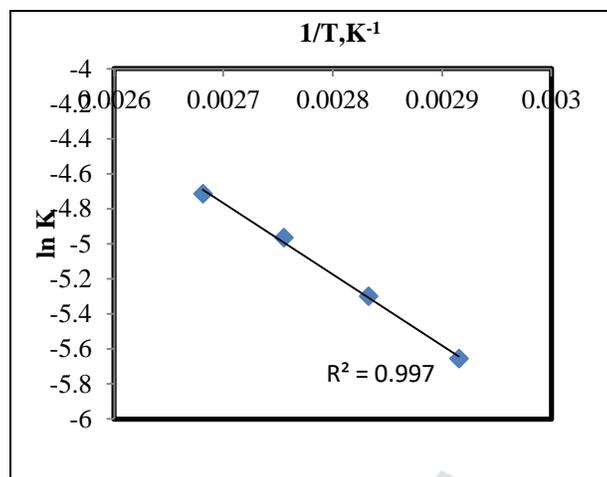


Figure 3.6 :Plot of lnK versus 1/T

The rate constants obtained from the above figure 3.5 were used to plot the Arrhenius equation, lnK versus 1/T figure 3.6 and the activation energy was found to be 33.76 kJ/mol with a regression coefficient of 0.997 signifying that the reaction is kinetically controlled.

Conclusion

The present work highlights the eco-friendly method for the synthesis of isoamyl acetate. The silica supported phosphomolybdic acid exhibited a 90% conversion at 100°C, 1:3 and 3w/w% catalyst loading. The development of kinetic model was done by considering the Langmuir–Hinshelwood model. Further, the activation energy value was reported based on the Arrhenius equation. The concepts of kinetics in hand with a choice of catalyst are useful for the development of an optimum continuous process for the synthesis of isoamyl acetate at large in industries at an economical way.

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