Heterogeneous Catalysed Esterification of Propionic Acid with n-Amyl Alcohol over a Microporous Cation-exchange Resin Dowex 50Wx4

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Kinetics of heterogeneous catalysed esterification of propionic acid with n-amyl alcohol was studied with a microporous cation-exchange resin catalyst, Dowex 50Wx4, in a stirred batch reactor to synthesise amyl propionate. Effects of various parameters such as speed of agitation, catalyst loading, and reaction temperature on reaction rate were investigated. The equilibrium conversion of propionic acid increased with in catalyst loading and reaction temperature. Stirrer speed had virtually no effect on the reaction rate under the experimental conditions. The apparent activation energy was found to be 43.167 kJmol⁻¹ for the formation of amyl propionate and the equilibrium constant, which is independent of temperature ranging from 318 to 348 K, was found to be 4.05. It was also observed that the initial reaction rate decreased with water concentrations and increased with that of acid and increased with that of alcohol linearly. The reaction was found to occur between an adsorbed acid molecule and a molecule of alcohol in the bulk and it was concluded that the reaction mechanism can be represented by Eley-Rideal model.

1. Introduction

Esterification of carboxylic acids with alcohols represents a well-known category of liquid-phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products. These ester products include environmentally friendly solvents, flavours, pharmaceuticals, plasticizers, polymeri-

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zation monomers and emulsifiers in the food, cosmetic and chemical industries [1]. Conversions for the esterification reactions have long been known to be limited by a slow reaction rate and the existence of reversible reactions. To accelerate the reaction rate, catalysts are always employed in a liquid-phase esterification. Despite the strong catalytic effect, the use of homogeneous catalysts, such as sulphuric acid and p-toluene sulfonic acid suffers from several drawbacks, such as the existence of side reactions, corrosion of the equipment and the need to deal with acidic wastes [2–5]. Homogeneous catalysts may also result in sulphur contamination of final ester product [5–6].

Under this situation the use of solid acid catalysts has received great attention in the past years. While there exist many solid acid catalysts, ion-exchange resins are the most commonly used and have been proved effective in liquid-phase esterification [7]. The use of ion-exchange resins as catalysts holds distinct advantages: (a) the purity of the products is higher, as the side reactions can be completely eliminated or are significantly less; (b) the catalyst can be easily removed from the reaction mixture by filtration; (c) the corrosive environment caused by the discharge of acid-containing waste is eliminated [4, 8]. Research in catalysis by ion-exchange resins undoubtedly is interesting, not only from a purely physicochemical point of view but also in terms of the advantages of these types of catalyst over the conventional ones [9].

Ion-exchange resins have been used in esterification [10] as well as the hydrolysis of methyl acetate in a catalytic distillation column [11]. Furthermore, they have been also used for the esterification of acetic acid with methanol [12, 13], liquid-phase esterification of lactic acid with iso-propyl alcohol [14], esterification of acetic acid with n-amyl alcohol [15], and esterification of propionic acid with methanol [16].

In the present study, the kinetic behaviour of the heterogeneously catalysed esterification of propionic acid with n-amyl alcohol was studied in stirred batch reactor using Dowex 50Wx4 (an acidic microporous-gel type cation-exchange resin) as a catalyst. In the previous work [17], basic investigation of intrinsic reaction kinetics in the presence of a heterogeneous catalyst was very limited for the present system since the reaction was regarded as homogeneous reaction. Because of their selective adsorption of reactants and swelling nature, these resins not only catalyse the esterification reaction but also affect the equilibrium conversion [2, 7]. In the literature, it was stated that the selective swelling of the polymer matrix may lead to values of the reactant to catalyst ratio different from those typically achieved in homogeneous catalytic systems under similar conditions. Moreover, the relative compositions of both reactants and products in the reaction locus (i.e. the polymeric resin) and in the liquid bulk are, in general, quite different. In particular, if these exhibit different affinities toward the resin, such that one of the reaction products tends to be selectively removed from the reaction locus, then the rate of the inverse reaction is minimised, and it is possible to achieve higher equilibrium conversions than those obtained with homogeneous catalysts [10]. As a result, this work was undertaken to find the kinetic model representing the esterification of propionic acid with n-amyl alcohol in the presence of heterogeneous catalyst, Dowex 50Wx4.

2. Experimental

2. 1. Chemicals and catalyst

n-Amyl alcohol (purity > 99.0 wt. %), propionic acid (purity > 99.0 wt. %) and 1,4-dioxane (purity > 99. wt. %) were obtained from Merck. Amyl propionate (purity > 99.0 wt. %) was obtained from Aldrich. They were used without further purification. The microporous sulfonic acid ion-exchange resin Dowex 50Wx4 purchased from Sigma-Aldrich was chosen as the catalyst in this work. It is cross-linked three-dimensional structure of polymeric material obtained by sulfonation of a copolymer of polystyrene and divinyl benzene [18]. Styrene copolymerized with a small amount of divinyl benzene at a low monomers dilution results in gel-type copolymers, which is characterized by a swollen state porosity. The pore size only depends on the proportion of divinyl benzene because of the restricted swelling of polymer structure by cross-linking. Therefore, the gel-type resins are completely ineffective as ion exchangers or catalysts in non-polar media. If the gel beads are dry, the polymer matrix collapses and the polymer chains will be as close as atomic forces allow [19, 20]. The acid catalytic activity of sulfonated polystyrene ion-exchange resins shows a pronounced dependence on the degree to which the polymer is sulfonated. This is, in part, due to the increased concentration of acid sites, but a more significant factor is that the acid strength also increases with the level of sulfonation. When the resins are used as anhydrous catalysts (as far as they can be), this increased acid strength is a direct result of structural features such as the degree of di-substitution, the presence of sulfone bridges and interactions between neighbouring groups [21]. For this reason, the catalyst washed with distilled water was dried in a vacuum oven (under 53.3 kPa) at 348 K, since drying at higher temperature involves the risk of loosing sulfonic acid sites in the form of SO₃ because of desulfonization of the polystyrene matrix of the catalyst [22]. The dried catalyst was stored in a desiccator until further use. The properties of the catalyst used for the present work are listed in Table 1.

2.2. Apparatus and procedure

Esterification of propionic acid with n-amyl alcohol over a fibrous polymersupported sulfonic acid catalyst, Dowex 50Wx4, was carried out in an isothermally operating glass reactor. The reactor was equipped with a heating jacket and a reflux condenser, which was placed on top of the reactor to prevent the escape of volatile components. The temperature was controlled within \pm 0.1 K by circulating water from a thermostat in to a cylindrical water-jacket of the

sulfonic acid functional group
styrene-divinylbenzene (gel- microporous)
20-50 mesh
570
423
4%

Table 1. Some physical and chemical properties of Dowex 50Wx4 catalyst.

reactor. In a typical run, dioxane and propionic acid were placed in the reactor. A known weight amount of the catalyst was added and the reactor content was well mixed. After a steady value of the desired temperature was attained, n-amyl alcohol, at the same temperature, was added and this was taken as zero time for a run. One millilitre of liquid sample was withdrawn from the reactor at regular intervals and the amount of unreacted acid was analysed by titration with 0.1 M NaOH. The liquid volume in all of the experiments was 0.100 dm³. A separate set of experimental runs under different conditions was performed to validate the model and its parameters.

The effect of water on reaction is important in esterification because H₂O is continuously produced as a product. Certainly, the presence of water promotes the reverse reaction; however, the effect of water on catalyst activity is even more critical [23]. Hence, kinetic measurements focused particularly on the initial period of reaction (<10 %) to minimize the impact of reverse hydrolysis. The values for initial reaction rates were calculated as $-(r_{A0}) = C_{A,0} (dX_A/dt)$, where $C_{A,0}$ is the initial concentration of the carboxylic acid and X_A is the conversion of the carboxylic acid. In addition, autocatalysis was negligible compared with Dowex 50Wx4 catalysis under the experimental conditions used; thus it did not have to be accounted for in the rate determinations.

3. Results and discussion

3. 1. Effects of speed of agitation and particle size

Sharma et al. observed that the internal mass-transfer resistance could be neglected and the conversion could be enhanced when a smaller particle size of the resin was used [23]. Yadav and Kulkarni stated that for average particle size less than 700 μ m there was no effect of particle size on the conversion of lactic acid [14]. The influence of external or pore diffusion can be neglected as reported in previous studies [8] To ensure the insignificance of the external mass-transfer resistance in kinetics measurements, experiments with different spinning speeds were carried out. From these literature assumptions, preliminary experiments were conducted varying the stirring speed, to quantify the influence of external resistances to heat and mass transfer. These experiments showed that there was



Fig. 1. Effect of stirring speed on conversion of propionic acid at 333 K (feed mole ratio: 1:1; catalyst: Dowex 50Wx4).

very little effect of speed of agitation in the range 300–700 rpm on the overall rate of the reaction (see Fig.1). A high degree of agitation was maintained in order to eliminate the liquid film resistance. It was found that stirrer speed of about 500 rpm was enough to keep all the catalyst particles in suspension and that the stirrer speed did not affect the rate of reaction until 700 rpm. Hence, in the range of stirrer speeds employed (300–700 rpm) the reaction rate was not affected by the liquid film resistance.

3.2 Effect of catalyst loading

In the absence of mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume. It was also stated that the reaction rate is linearly depended on resin concentration [8]. Catalyst loading was varied from 0.7 % to 2.0 % (w/w) (i.e. weight of catalyst / weight of propionic acid) at a temperature of 333 K, feed mole ratio (alcohol to acid) of 1:1, and stirrer speed of 700 rpm. It is clear from Fig. 2 that the conversion of propionic acid increases with an increase in catalyst concentration. With an increase in the number of resin functional groups, the concentration of the carbonium ion formed increased. With the utilisation of cationic resins a relatively high yield of ester was assumed [24]. The higher the catalyst loading, the



Fig. 2. Effect of catalyst loading on conversion of propionic acid at 333 K (feed mole ratio: 1:1; catalyst: Dowex 50Wx4; stirrer speed: 700 rpm).

faster the rate at which equilibrium conversion was reached because of the increase in the total number of available active catalytic sites for the reaction.

3.3 Effects of reactant and product concentrations

The calculation of kinetic parameters for heterogeneous acid catalyst is complicated because of the complex catalyst surface-adsorbate interactions [25]. Initial reaction rates were examined by varying the concentration of one reactant while fixing that of the other at 1.0 molL⁻¹. The results obtained experimentally are illustrated in Figs. 3–5.

As seen in Fig. 3, the initial reaction rate, measured at different acid concentrations, increased linearly with low acid concentrations, but it was nearly independent of acid concentrations at high levels. Fig. 4 indicated that the initial reaction rate increased linearly with alcohol concentration. On the other hand, we observed from Fig. 5 that, for fixed concentrations of propionic acid and namyl alcohol (1.0 M) the rate decreases with increasing concentration of water. The type of dependence of this rate suggests that water is adsorbed on the catalyst surface [26]. In the subsequent tests, it was determined that the adsorption of amyl propionate and solvent (dioxane) could be negligible. From these analyses, it was concluded that the reaction mechanism can be represented by Eley-Rideal model, that is, the reaction takes place between adsorbed molecules of acid and the molecules of alcohol free in the bulk solution. This model is derived based on the assumption that the rate-limiting step is the surface reaction between an adsorbed molecule and molecule in the bulk. In this mechanism, propionic acid molecules are adsorbed on the active site of the resin and protonated first



Fig. 3. Effect of propionic acid concentration on initial reaction rate at different temperatures (catalyst loading: 1.4 % (w/w); catalyst: Dowex 50Wx4; stirrer speed: 700 rpm; $C_{B0} = 1.0 \text{ mol } L^{-1}$; $C_{E0} = C_{W0} = 0$).



Fig. 4. Effect of n-amyl alcohol concentration on initial reaction rate at different temperatures (catalyst loading: 1.4 % (w/w); catalyst: Dowex 50Wx4; stirrer speed: 700 rpm; $C_{A0} = 1.0 \text{ mol } L^{-1}$; $C_{E0} = C_{W0} = 0$).

and then reacted with n-amyl alcohol molecules in the bulk liquid. The products formed, namely, amyl propionate and water, are then desorbed from the surface.

3.4 Reaction mechanism

The preliminary mathematical modelling of the observed esterification kinetics was based on second order kinetics, which principally could be applied to both homogeneous and heterogeneous catalyst [27]. This acid catalysed esterification reaction is an equilibrium limited chemical reaction:



Fig. 5. Effect of water concentration on initial reaction rate at different temperatures (catalyst loading: 1.4 % (w/w); catalyst: Dowex 50Wx4; stirrer speed: 700 rpm; $C_{A0} = C_{B0} = 1.0 \text{ mol } L^{-1}$; $C_{E0} = 0$).



Scheme 1.

$$R - C + HO - R_1 \xrightarrow{k_2}_{k_2} R - C - O - R_1 \xrightarrow{k_3}_{K_3} R - C - O - R_1 + H_2O$$

Scheme 2.

$$\underbrace{CH_3CH_2COOH}_{(A)} + \underbrace{CH_3(CH_2)_4OH}_{(B)} \underbrace{\xrightarrow{k_x}}_{(k_x^{-1})} \underbrace{CH_3(CH_2)_4COOCH_2CH_3}_{(E)} + \underbrace{H_2O}_{(W)} (1)$$

The sulfonic acid groups (HSO_3^-) on a heterogeneous catalyst or H^+ in a homogeneous catalyst (e. g. H_2SO_4 , HCl) initiate the esterification reaction by donating a proton to the carboxylic acid molecule (see Scheme 1).

After the proton transfer, the carboxylic acid is accessible for a nucleophilic attack by the hydroxyl group from the alcohol (R_1OH), and the reaction continues with water elimination: (see Scheme 2).

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Scheme 3.

Finally, the catalyst is recovered (see Scheme 3).

The proton-donating step is usually assumed to be rapid, while the nucleophilic substitution is slow. The rate-determining step gives the overall rate equation for the reaction (1)

$$-r_{A} = (k_{S} C_{A} C_{B} - k_{S^{-1}} C_{E} C_{W})$$
⁽²⁾

where k_S and $k_{S^{-1}}$ are the forward and the reverse rate constants, respectively and C_i denotes concentration for component i.

Depending on the experimental results given in section (3.3), Eq. (2) can be arranged according to Eley-Rideal mechanism as follows:

$$-r_{A} = \frac{k_{f} (m/V) (C_{A}C_{B} - C_{E}C_{W}/K_{e})}{1 + K_{A}C_{A} + K_{W}C_{W}}$$
(3)

where subcripts A, B, E and W refer to acid, alcohol, ester and water, respectively. k_f is lumped rate constant of the reaction, K_e is the equilibrium constant of the reaction. K_A and K_W are the adsorption equilibrium constants for the acid and water, m is the quantity of dry resin and V is the volume of the reaction mixture.

For a molar ratios of $C_{B,0}/C_{A,0} = M$ and $C_{W,0}/C_{A,0} = N$, Eq. (3) can be expressed in terms of propionic acid conversion and it becomes

$$-r_{A0} = \frac{dX_A}{dt} = \frac{k_f C_{A0} m/V [(1-X_A)(M-X_A) - (X_A(N+X_A)/K_e]]}{[1+K_A C_{A0}(M-X_A) + K_W C_{A0}(N+X_A)]}$$
(4)

By using the "Method of Averages" [28], k_f , K_A and K_W were calculated for different temperatures and these results are given in Table 2.

3.5 Effect of temperature

The study on the effect of temperature is very important for a heterogeneously catalysed reaction as this information is useful in calculating the apparent activation energy. Moreover, the intrinsic rate constants are strong functions of temperatures [4]. The effect of temperature on the rate of reaction was studied by conducting the reactions at 318, 333 and 348 K under the similar conditions (a feed mole ratio of 1:1, a stirrer speed of 700 rpm, and at 1.4 % (w/w) Dowex



Fig. 6. Effect of temperature on conversion of propionic acid at a catalyst loading of 1.4 % (w/w) (feed mole ratio: 1:1; catalyst: Dowex 50Wx4; stirrer speed: 700 rpm).



Fig. 7. Arrhenius plot of esterification of propionic acid with n-amyl alcohol (T = 318–348 K; $C_{A0} = C_{B0} = 1.0 \text{ molL}^{-1}$; stirrer speed: 700 rpm; catalyst loading: 1.4 % (w/w)).

50Wx4 catalyst loading). Fig. 6 shows that the higher temperature yields the greater conversion of propionic acid at a fixed contact time.

The dependence of forward reaction rate constant, k_f , on temperature was determined from Arrhenius equation, Eq. (5). This is to be shown in Fig. 7.

$$k_{f} = \dot{A} \cdot e^{-E_{a}/RT} \tag{5}$$

The value of apparent activation energy, E_a and pre-exponential factor, *A* were obtained from least square fit of Eq. (5) to the data given in Table 2 and the computed values are given in Table 3. The reaction equilibrium constant, K_e , was found to be 4.05, independent of temperature ranging from 318 to 348 K, in other words, the change in the value of K_e , was included in the experimental error of it. The dependence of adsorption constants, K_A and K_W , on temperature is related by [29]:

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T (K)	$k_f (L^2(g dry resin)^{-1}mol^{-1}min^{-1})$	K _A (Lmol ⁻¹)	K _W (Lmol ⁻¹)
318	0.000086	0.2787	4.5558
333	0.000201	0.2148	3.0744
348	0.000351	0.1661	2.1747

Table 2. Parameters for E-R model used to fit the experimental data.

Table 3. Thermodynamic results obtained from for amyl propionate esterification.

E _a (kJmol ⁻¹)	\dot{A} (L ² (g dry resin) ⁻¹ mol ⁻¹ min ⁻¹)	$\Delta H^0(kJmol^{-1})$	$\Delta S^{0}(kJmol^{-1}K^{-1})$
43.167	1093.676	-15.872(foracid)	-0.060(foracid)
		-22.694(forwater)	-0.059(forwater)



Fig. 8. Comparison of experimental data with values predicted by Eq. (4) for esterification of propionic acid with n-amyl alcohol on Dowex 50Wx4 loading of which is 1.4 % (w/w); symbol represents the experimental data; dashed lines represent the model prediction (T = 333 K; feed mole ratio: 1:1; stirrer speed: 700 rpm; M = 1; N = 0; K_e = 4.05).

$$K = \exp\left[-\frac{\Delta G^{0}}{RT}\right] = \exp\left[\frac{\Delta S^{0}}{R}\right] \exp\left[-\frac{\Delta H^{0}}{RT}\right]$$
(6)

The values of ΔS^0 and ΔH^0 were also obtained by least square fit of Eq. (6) and the values are given in Table 3. The heats of adsorption for propionic acid and water were found to be negative, as they are exotermic process, and therefore K_A and K_W decrease with the increase of temperature.

Using numerical integration (Runga-Kutta), propionic acid conversion at a given time can be predicted from Eq. (4) under the condition of 333 K; $M = C_{B0}/C_{A0} = 1$; $N = C_{W0}/C_{A0} = 0$; $K_e = 4.05$; m/V = 1 g dry resin/0.1L; $C_{A0} = 1.0$ mol L⁻¹. The dotted lines in Fig. 8 give the prediction of reaction conversion based on Eq. (4). According to this figure, Eq. (4) satisfactorily represents the esterification of propionic acid and n-amyl alcohol on Dowex 50Wx4.

4. Conclusion

In this work, the catalytic performance of the Dowex 50Wx4 microporous cation exchange resin was evaluated for the esterification of propionic acid with namyl alcohol. Kinetic and thermodynamic parameters such as activation energy, adsorption energies for propionic acid and water were obtained for the model reaction. As for the reaction equilibrium constant (K_e), which is independent of temperature ranging from 318 to 348 K, was determined to be 4.05.

The conversion of propionic acid increased with an increase in the amount of catalyst. But the equilibrium conversion was not affected. Therefore, the time required to reach the reaction equilibrium was shortened due to the increase in the total number of acid sites available [30].

The esterification reaction on Dowex 50Wx4 appears to involve single-site catalysis with a probable rate-controlling Eley-Rideal surface reaction and this kinetic model successfully predicts the esterification rate of Dowex 50Wx4 as reaction progresses.

In the esterification of propionic acid and n-amyl alcohol, a good agreement between the calculated curve and the experimental points is observed. It is concluded that Dowex 50Wx4 is an influent catalyst to accelerate the esterification reactions.

Appendix

Nomenclature

A, B, E, Wpropionic acid, n-amyl alcohol, amyl propionate and water, respectively

r_{A0}initial reaction rate of propionic acid ksforward reaction rate constant k_{S}^{1} reverse reaction rate constant mquantity of dry resin Vreaction mixture volume $C_{A,0}$ initial concentration of propionic acid (mol. L⁻¹) $C_{B,0}$ initial concentration of n-amyl alcohol (mol. L⁻¹) $C_{E,0}$ initial concentration of amyl propionate (mol. L⁻¹) $C_{W,0}$ initial concentration of water (mol. L⁻¹) $k_{\rm f}$ lumped rate constant (L². (g dry resin)⁻¹. mol⁻¹. min⁻¹) Ke equilibrium constant of the reaction K_A adsorption equilibrium constant for propionic acid (L. mol⁻¹) K_{w} adsorption equilibrium constant for water (L. mol⁻¹) X_Aconversion of propionic acid A Arrhenius preexponential factor (L^2 . mol⁻¹. min⁻¹) E_a apparent activation energy (kJ. mol⁻¹) Ttemperature (K)

Rgas constant (kJ. mol^{-1} . K^{-1})

 ΔG^0 adsorption free energies for propionic acid and water (kJ. mol⁻¹) ΔS^0 adsorption entropies for propionic acid and water (kJ. mol⁻¹. K⁻¹) ΔH^0 heats of adsorption for propionic acid and water (kJ. mol⁻¹) ttime (min)

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