Kinetics of Synthesis of Isobutyl Propionate over Amberlyst-15

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The esterification of propionic acid with isobutanol in the presence of Amberlyst-15 as a catalyst was studied. Isobutyl propionate synthesized in this reaction has the fragrance of rum and is used in the food industry. The experiments were carried out in a stirred batch reactor at temperatures from 318 K to 348 K. As a solvent, 1,4 dioxan was used. The effects of the amount of catalyst used, the reaction time, the stirring speed, and the reaction temperature on the synthesis of isobutyl propionate were investigated. It was observed that solid-liquid external mass transfer resistance resulting from various stirring speeds was absent. It was also found that the reaction depended on temperature. A pseudohomogeneous model for Amberlyst-15 was developed from the experimental data. The activation energy and the equilibrium constant of this reaction were calculated to be 52.03 kJ.mol^{-1} and 5.19, respectively. The expression of the reaction rate as a function of temperature was determined for the synthesis of isobutyl propionate.

Key Words: Esterification, pseudohomogeneous kinetics, isobutyl propionate, ion-exchange resin, Amberlyst-15.

Introduction

The low molecular weight organic esters have pleasant odors and are used in the food industry for artificial flavors and fragrances.[1−7] Isobutyl propionate is one of them. It has an ethereal, rum-like, fruity odor, and occurs naturally in apples, grapes, melons, and rum. Isobutyl propionate gives a rum flavor to beverages, candies, and baked goods. Isobutyl propionate, $C_2H_5COOC_4H_9$, is synthesized by esterification of propionic acid with isobutyl alcohol.

$$C_3H_7COOH + C_4H_9OH \Leftrightarrow C_2H_5COOC_4H_9 + H_2O \tag{1}$$
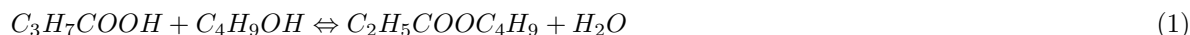
The reaction of Eq. (1) proceeds very slowly in the absence of acid catalysis. Therefore, both homogeneous and heterogeneous catalysis can be employed. Although homogeneous catalysts such as sulfuric acid, p-toluene sulfuric acid, and hydrochloric acid have a strong catalytic effect, they can cause some problems such as the formation of side reactions resulting in a corrosive environment by the discharge of

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acid-containing waste.[8−12] Heterogeneous catalysts such as zeolites, ion exchange resins, and acidic clay catalysts are gaining importance for high purity of products, because they are easily removed from the reaction mixture and have lower corrosive effects.[13,14]

Most reactions catalyzed by ion exchange resins can be classified as either quasihomogeneous or quasiheterogeneous.[15,16] The kinetics of this model reaction catalyzed by Amberlyst-15 were described in previous investigations with both a quasihomogeneous and a quasiheterogeneous model.[11,17−20]

Theory

For isobutyl propionate synthesis, it was shown that a pseudohomogeneous model is sufficient for small amounts of water in the reactor.[21,22] Thus, pseudohomogeneous models were used to describe heterogeneously by ion-exchange resins catalyzed esterification reactions.

Kinetic model

Esterification reactions are known to be second-order reversible reactions. Therefore, for the bimolecular-type second-order reactions,

$$A + B \rightleftharpoons E + W \tag{2}$$

with the restrictions that $C_{A0} = C_{B0}$ and $C_{E0} = C_{W0} = 0$, the rate equation can be written as

$$-r_B = -\frac{dC_B}{dt} = C_{B0}\frac{dX_B}{dt} = k_1 C_A C_B - k_2 C_E C_W$$
$$= k_1 C_{B0}^2 (1 - X_B)^2 - k_2 (C_{B0} X_B)^2 \tag{3}$$

where A, B, E, and W refer to propionic acid, isobutyl alcohol, isobutyl propionate, and water, respectively.

At the equilibrium, $-r_B = 0$. Hence, from the above equations, we find the fractional conversion of B at the equilibrium conditions by

$$K = \frac{C_{Ee}C_{We}}{C_{Ae}C_{Be}} = \frac{X_{Be}^2}{(1 - X_{Be})^2} \tag{4}$$

and the equilibrium constant by

$$K = \frac{k_1}{k_2} \tag{5}$$

Combining the above 3 equations, in terms of the equilibrium conversion, we obtain

$$\frac{dX_B}{dt} = k_1 C_{B0} \left[(1 - X_B)^2 - \left(\frac{1 - X_{Be}}{X_{Be}} \right)^2 X_B^2 \right] \tag{6}$$

With conversions measured in terms of X_{Be}, this may be indicated as a pseudosecond-order reversible reaction which, on integration, gives

$$\ln \left[\frac{X_{Be} - (2X_{Be} - 1)X_B}{X_{Be} - X_B} \right] = 2k_1 \left(\frac{1}{X_{Be}} - 1 \right) C_{B0} t \tag{7}$$

Temperature and reaction rate

We can examine the variation of the rate constant with temperature by an Arrhenius' law relationship.

$$k_1 = k_1^0 \exp\left(\frac{-E_A}{RT}\right) \tag{8}$$

This is conveniently determined by plotting $\ln k_1$ versus $1/T$.

Experimental

Chemicals

Propionic acid of 99% purity (Merck) and isobutanol of 98.5% purity (Merck) were used in the experiments and 1,4 Dioxan of 99.8% purity was purchased from Carlo Erba. All chemicals were used without further purification. The macroreticular ion exchange resin, Amberlyst-15, was used in this study. This resin, manufactured by Rohm-Haas, is a strongly acidic and macroreticular polymeric material based on cross-linked styrene divinyl benzene copolymers. A pretreatment procedure was applied to the catalyst before use. The catalyst was washed with methanol and water to separate the impurities. The washed catalyst was kept in a vacuum oven at 348 K until the water content was completely removed. The physical properties of the catalyst employed for this reaction are listed in the Table.

Table. Physical properties of Amberliyst-15 cation exchanger.

Ionic form as shipped	hydrogen
Concentration of active sites	$\geq$ 1.7 eq/L; $\geq$ 4.7 eq/kg
Moisture holding capacity	52 to 57% (H^+ form)
Shipping weight	770 g/L
Particle size	0.600 to 0.850 mm
Surface area	53 m^2/g
Average pore diameter	300 Å
Total pore volume	0.40 mL/g
Max. operating temperature	120 °C (250 °F)

Apparatus

The experiments were carried out in a stirred batch reactor consisting of a water jacket with 400 mL capacity. The reaction temperature in the reactor was controlled within $\pm$ 0.1 K by circulating water from a thermostatic water bath (JULABO). A reflux condenser was fitted to the reactor to prevent a massive loss of the reaction mixture. The reactor content was stirred by a magnetic stirrer at 1000 rpm.

Experimental procedure

All catalysts were dried at 75 °C under vacuum for 48 h before use. Catalyst, isobutanol, and solvent (1,4 Dioxan) were loaded into the reactor, which was heated to the desired temperature. Propionic acid, at the same temperature, was added finally. This was taken as the starting time of the reaction (zero time) for a run. For kinetic measurements, samples of the reaction mixture were collected at specified intervals.

The experiments of the equilibrium conversion were carried out in the temperature ranging between 318 and 348 K at molar feed ratio of 1:1 and 1000 rpm in the presence of Amberlyst-15 as a catalyst. Samples of the reaction mixture were collected at specified intervals. After a steady value of the conversion was attained, the equilibrium constants were determined in these temperature intervals.

Analysis

An HP 6890 Gas Chromatography with Flame Ionization Detector (FID) was used to analyze the collected samples. Isobutanol, dioxan, propionic acid, and isobutyl propionate were separated in DB-WAX (30 m × 0.53 mm column). A Schott TA05 Plus Karl Fischer titrator was used to analyze the water content of the samples.

Results and Discussion

The equilibrium constant was experimentally determined using Amberlyst-15. It was found that the equilibrium constant is independent of temperature ranging from 318 to 348 K. Using Eq. (4), the apparent equilibrium constant obtained from the equilibrium conversion was experimentally determined to be 5.19.

The experiments of reaction kinetics were conducted under similar conditions of reactant concentration (or mole ratio), catalyst loading, particle size, speed of agitation, and the type of catalyst except for the reaction temperature. The experiments were carried out in a differential reactor. Thus, the effect of the parameter on the initial reaction rate was obtained in Figures 1 and 2.
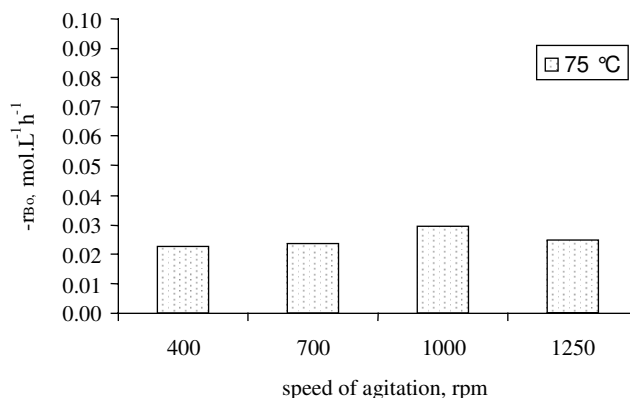

Figure 1. Effect of speed of agitation (Catalyst loading=8 g-dry resin/L, mole ratio (propionic acid/isobutanol) = 1:1, T = 348 K, speed = 1000 rpm).

Effect of speed of agitation and particle size

In order to check the influence of external diffusion resistance, the experiments were conducted at different stirrer speeds, namely 400-1250 rpm at constant values of reaction temperature and catalyst concentration (Figure 1). In this range of stirrer speed, the experiments showed that there was very little effect of the speed of agitation, that is, no influence on external diffusion resistance from the bulk liquid to the surface of the catalyst was observed. Hence, all the experiments were conducted at a stirrer speed of 1000 rpm.

Furthermore, it was reported that there is no influence of the interparticle pore diffusion and interparticle transport can be neglegible.[23]
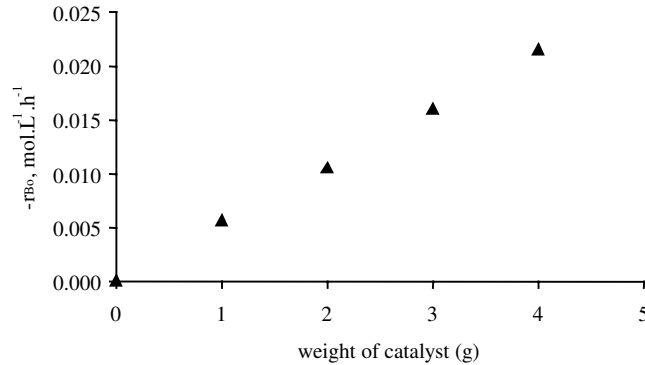

Figure 2. Effect of the catalyst loading (Speed of agitation = 1000 rpm, mole ratio (propionic acid/isobutanol) = 1:1, T = 333 K).

Effect of catalyst loading

The catalyst loading was varied from 1 to 4 g dry-resin at a temperature of 333 K, feed mole ratio of 1:1, and stirrer speed of 1000 rpm (see Figure 2).

Reaction kinetics

The esterification reaction was kinetically controlled since the external mass transfer resistance and the interparticle diffusion resistance were absent. The catalyst used is a macroporous ion exchange resin. In a macroporous resin, the reactants are able to diffuse into the pores without any resistance.[24] Therefore, sorption effects can be neglected and a pseudohomogeneous model should be sufficient. The experimental data collected at temperatures from 318 to 348 K were used to plot the left-hand side (LHS) of Eq. (7) versus time to get a straight line passing through the origin (Figure 3). From the slopes of these lines given in Figure 3, the forward reaction rate constant (k_1) was found to be 4.365×10^{-3}, 9.997×10^{-3}, and 23.85×10^{-3} L.mol^{-1}.h^{-1} at 318, 333, and 348 K, respectively.
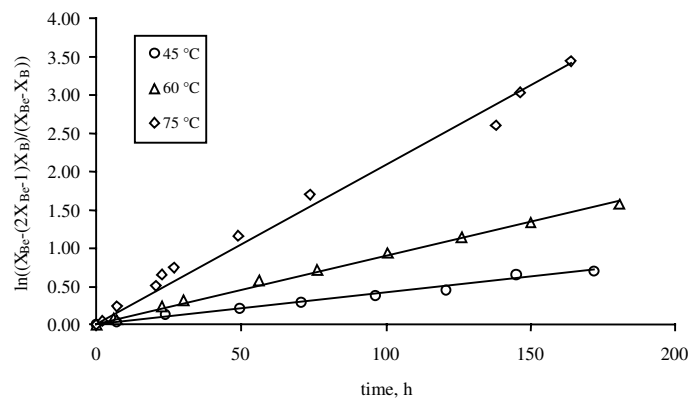

Figure 3. LHS of Eq. (7) vs. time at different temperatures (Speed of agitation = 1000 rpm, mole ratio (propionic acid/isobutanol) = 1:1, Catalyst loading = 8 g-dry resin/L).

Using these values in Arrhenius Eq. (8), -lnk was plotted against 1/T (Figure 4). The activation energy was obtained as 52.03 kJ.mol^{-1}. The temperature dependency of the rate constant was calculated to be

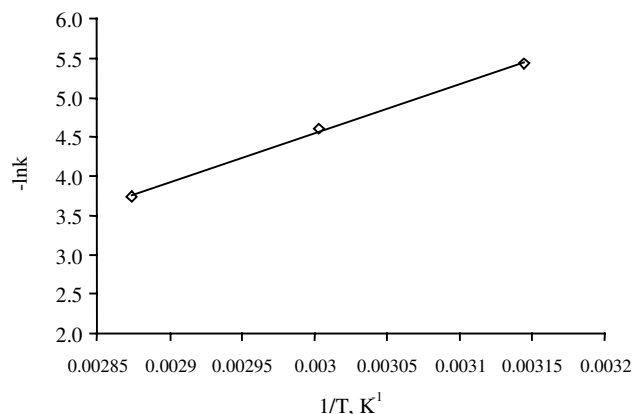$$k = \exp\left(14.23 - \frac{6258}{T}\right) \qquad (9)$$

Figure 4. Arrhenius plot of -lnk vs. 1/T. (Speed of agitation = 1000 rpm, mole ratio (propionic acid/isobutanol) = 1:1, Catalyst loading = 8 g-dry resin/L).

Conclusions

The kinetic behavior of the esterification of propionic acid with isobutanol in the temperature ranging between 318 and 348 K and at molar feed ratio of 1:1 was investigated experimentally in a stirred batch reactor using Amberlyst-15 as a catalyst. This reaction was intrinsically kinetically controlled. A pseudohomogeneous kinetic model was employed to fit the experimental data.

The activation energy was found to be 52.03 kJ.mol^{-1}. It was also shown that the temperature dependency of the constants appearing in Eq. (8) can be given by Eq. (9). The equilibrium constant, which is independent of temperature ranging between 318 and 348 K, was found to be 5.19.

Acknowledgments

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