A preliminary evaluation of a continuous-flow reactor for liquid–liquid–solid phase-transfer catalyzed synthesis of n-butyl phenyl ether

Hsu-Chin Hsiao,1∗ Wei-Chi Li2 and Hung-Shan Weng2
1Department of Chemical Engineering, Tung Fang Institute of Technology, Kaohsiung, Taiwan 829, China
2Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, China

Abstract: This study evaluates the feasibility of using a continuous-flow stirred vessel reactor (CFSVR) to synthesize n-butyl phenyl ether (ROPh) from n-butyl bromide (RBr) and sodium phenolate (NaOPh) by liquid–liquid–solid phase-transfer catalysis (triphase catalysis). The factors affecting the preparation of triphase catalysts, the etherification reaction in a batch reactor, and the performance in a CFSVR were investigated. The kinetic study with a batch reactor indicated that when the initial concentration of NaOPh or RBr was high, the conversion of RBr would depend on the initial concentration of both RBr and NaOPh. The reaction can be represented by a pseudo-first-order kinetic model when the concentration of NaOPh is in proper excess to that of RBr, and the apparent activation energy is 87.8 kJ mol$^{-1}$. When the etherification reaction was carried out in the CFSVR, the catalyst particles did not flow out of the reactor, even at a high agitation speed. The conversion of RBr in the CFSVR was, as predicted, lower than that in the batch reactor, but was higher than the theoretical value because the dispersed phase is not completely mixed.

Keywords: triphase catalyst; phase-transfer catalysis; continuous-flow reactor; n-butyl phenyl ether; n-butyl bromide; sodium phenolate

1 INTRODUCTION

Since polymer-supported catalysts were first utilized in phase-transfer catalysis by Regen$^1$ in 1975, tremendous research has been reported. However, nearly all of these triphase catalytic reactions, even for industrial applications, have been performed in batch reactors. Although a few studies have addressed the use of a reactor with continuous inlet and outlet streams,$^2–^4$ these particular reactors, in fact, cannot be called continuous-flow reactors. Moreover, the apparatus and systems are more complicated than is desirable. Therefore, the present investigation is aimed at designing a simple continuous-flow reactor system for triphase catalysis, which can be easily scaled up for industrial operations.

In a study on the monoalkylation of phenylacetoni- trile with n-butyl bromide using polymeric catalysts containing quaternary ammonium groups or poly(ethylene glycols) Ragaini et al$^5$ used a fixed-bed reactor which was put inside or outside a mixing chamber installed with different mixers. The mixed solution was pumped through the fixed-bed reactor and back to the mixing chamber continuously until the conversion of phenylacetonitrile detected in the mixing chamber reached a certain value. Although the fixed-bed reactor was operated under continuous flow conditions, the whole system was in a closed mode.

Our laboratory evaluated the feasibility of reusing a third liquid phase catalyst in a continuous-flow stirred vessel reactor for the reaction between n-butyl bromide and sodium phenolate catalyzed by tetra-n-butyrammonium bromide. We indicated that, while most of the catalyst stays inside the reactor, a small fraction of soluble catalyst flows out along with the aqueous and organic phases. The loss of catalyst caused a small decline in conversion.$^5$

When the density of polymer-supported catalyst particles in the liquid–liquid–solid phase-transfer catalytic system is in between those of organic and aqueous solutions, the catalyst particles can suspend in the reacting fluids and never settle down to the bottom of the reactor or flow out from the reactor, hence continuous operation of a liquid–liquid–solid system becomes possible. In this study, therefore, we investigated the feasibility of using a continuous-flow stirred vessel reactor (CFSVR) for a triphase

∗Correspondence to: Hsu-Chin Hsiao, Department of Chemical Engineering, Tung-Fang Institute of Technology, Kaohsiung, Taiwan 829, China
E-mail: hchsiao@mail.tf.edu.tw
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catalytic reaction. The same reaction between n-butyl bromide (RBr) and sodium phenolate (NaOPh) is employed as a model reaction. A polymeric catalyst containing quaternary ammonium groups (QBr\(_n\)) was used as the catalyst. The overall reaction is RBr + NaOPh → ROPh + NaBr. The reaction mechanism is represented in Scheme 1.

This mechanism is similar to that of tri-liquid-phase catalysis.\(^6\)\(^7\) When the organic and aqueous reactants are immiscible in the aqueous and organic phases, the substitution reaction (Eqn (I)) and ion-exchange (Eqn (II)) mainly take place on the catalyst surface alternately. In addition, the hydrophilicity (or lipophilicity) of the catalyst is a crucial factor for influencing the rates of Eqns (I) and (II).

However, this nucleophilic reaction may occur without catalyst, though it is relatively slow (Scheme 2):

For examining the feasibility of using a CFSVR for triphase catalysis, the triphase catalyst was prepared first by immobilizing tri-n-butylamine onto chloromethylated polystyrene. Then, a batch reactor was employed to collect some basic kinetic data and the factors influencing the conversion were investigated. Subsequently, a CFSVR was operated under the conditions determined by referring to the results obtained from the batch reactor, and the results were discussed.

2 EXPERIMENTAL

2.1 Chemicals

Chloromethylated polystyrene was obtained from Fluka AG, Chemische Fabrik (Switzerland). It contains 2 mol % of divinylbenzene and 4.3 meq g\(^{-1}\) of chloromethylated groups. Its degree of crosslinking is 2.5% and the particle size is 200–400 mesh. Sodium phenolate was purchased from Merck Schuchardt (Germany) and n-butyl bromide, tri-n-butylamine, and N\(_2\)N-dimethylformamide (DMF) were obtained from Lancaster Synthesis Ltd (England). Toluene, n-heptane, n-dodecane, methanol, and acetone were obtained from Tedia Company, Inc (USA). All chemicals were more than 98% pure and were used as supplied.

2.2 Methods and procedure

2.2.1 Immobilization of tri-n-butylamine

One gram of chloromethylated polystyrene (support) was swelled in 5 cm\(^3\) of DMF in a Pyrex test tube (2.0 cm internal diameter, 5.0 cm high) for 30 min and then 8.6 mmol (unless specified) of tri-n-butylamine was added to the mixture. The tube contents were subsequently purged with inert nitrogen gas, sealed in with a screw cap, placed in a water bath maintained at a fixed temperature to start the immobilization reaction, and withdrawn at a specified time. The resultant particles were filtered, washed successively with methanol, acetone, and anhydrous methanol, and dried under vacuum at 50 °C for 2 h, to obtain the triphase catalyst used in this study. In addition, the chloride ion content inside the catalyst, which is equal to the content of tri-n-butylamine immobilized on the support, was determined by the Volhard method. The chloride ion density in catalyst was found to be 1.738 meq g\(^{-1}\).

2.2.2 Triphase catalysis in a batch reactor

A 125-cm\(^3\) three-neck round-bottom flask was used as a laboratory batch reactor. Known quantities (18–118 mmol) of NaOPh and triphase catalyst (0–3.5 g), 25 cm\(^3\) of water, and 25 cm\(^3\) of toluene were introduced into the reactor, maintained at a fixed temperature using a water bath. The mixture was stirred by a magnetic bar for 30 min with an agitation speed of 1000 rpm. To start a kinetic run, a measured quantity (9–54 mmol) of RBr solution (containing 23% n-dodecane as an internal standard) was added to the reactor. At preset times, the stirrer was turned off temporarily and 0.1 cm\(^3\) of organic solution was pipetted out and poured into a test tube containing 4 cm\(^3\) of cooling water. The tube was subsequently shaken and then allowed to stand until a complete...
phase separation had occurred. After that, 0.0005 cm$^3$ of organic solution was removed from the tube and analyzed using a gas chromatograph (Shimadzu GC-14A with FID) having a column (1/8" ID and 10' long) packed with Chromosorb W (80–100 mesh) coated with 10% SE-30.

2.2.3 Triphase catalysis in a continuous-flow stirred vessel reactor (CFSVR)

A schematic representation of the CFSVR used in this study is shown in Fig 1. The effective volume is about 250 cm$^3$. The organic solution was admitted at the bottom while the aqueous solution was fed in at the top. The catalyst particles reside near the interface between the organic and aqueous phases when the solutions are not agitated and do not flow out when the solutions are agitated. Notably, the effective reaction volume for the organic or aqueous phase is nearly 100 cm$^3$ when 12.5 g of triphase catalyst is added. The CFSVR was operated according to the following procedure.

1. An aqueous solution containing sodium phenolate (NaOPh) and an organic solution consisting of RBr, $n$-dodecane, and toluene (as a solvent) were prepared and stored in the reservoirs.
2. Aliquots, 110 cm$^3$ each, of the prepared aqueous and organic solutions, and a specified amount of triphase catalyst were admitted into the reactor.
3. After the conversion reached the predicted value, at about 50 min, the prepared aqueous and organic feed solutions were continuously fed into the reactor and the aqueous and organic solutions in the reactor were withdrawn from it at the same volumetric rate. The concentration of RBr in the outlet organic solution was analyzed every 2 hs. Three samples (0.1 cm$^3$ each) were taken each time.

2.3 Definition

The conversion of RBr is defined as follows:

\[ X = 1 - \frac{[RBr]}{[RBr]_0} \quad \text{for batch reactor;} \]

\[ X = 1 - \frac{[RBr]}{[RBr]_i} \quad \text{for CFSVR} \]

where [RBr] represent the concentration of $n$-butyl bromide in the organic phase, and the subscripts o and i stand for the initial and inlet conditions, respectively. The concentration of RBr was determined from the calibration curves relating the G.C. areas and weight ratios of RBr to the internal standard ($n$-dodecane).

2.4 Rate expression

The rate expression for the etherification reaction in a triphase catalytic system has been derived by Wang and Yang.\cite{8} They have also indicated that the overall reaction rate of the organic reactant with the aqueous reagent can be expressed using a pseudo-first-order kinetic model when excess nucleophile is used. Because the organic reactant used in the present study, $n$-butyl bromide (RBr), undergoes a similar substitution reaction, the same reaction rate expression may be tested, ie the overall reaction rate of RBr per volume of the organic phase may be expressed as:

\[ -r_{RBr} = k[RBr] \quad (1) \]

where $k$ is the apparent reaction rate constant.

When this reaction is carried out in a batch reactor, the diminution rate of RBr per volume of the organic phase with time ($t$) can be expressed as:

\[ -\frac{d[RBr]}{dt} = -r_{RBr} = k[RBr] \quad (2) \]

Integrating Eqn (2) yields:

\[ -\ln \frac{[RBr]}{[RBr]_o} = -\ln(1 - X) = kt \quad (3) \]

If a linear relationship of $-\ln(1 - X)$ and $t$ is obtained, we may claim that the reaction of RBr with OPh$^-$ can be represented by a pseudo-first-order kinetic model and the value of $k$ can be determined from the slope of the straight line.

Figure 1. Schematic diagram of the continuous-flow stirred vessel reactor (CFSVR). Unit of scale = cm.
2.5 Equations for predicting conversion of RBr

2.5.1 Batch reactor
The equation for predicting $X$ in a batch reactor can be obtained by rewriting Eqn (3):

$$X = 1 - \exp(-kt)$$

2.5.2 Continuous-stirred tank reactor (CSTR)
The design equation for a perfectly mixed CSTR is:

$$X = \frac{V(-r_{fA})}{F_{A0}} = \frac{V(-r_{fA})}{v_{org}C_{A0}} = \frac{\tau(-r_{fA})}{C_{A0}}$$

where $V$ is the reaction volume, $-r_{fA}$ the reaction rate of reagent A (evaluated at the exit conditions), $F_{A0}$ the entering molar flow rate of reagent $A$, $v_{org}$ the volumetric flow rate, $C_{A0}$ the inlet concentration of $A$, and $\tau = V/v_{org}$.

For an irreversible first order reaction without volume change during the course of the reaction, $-r_{fA} = kC_A = kC_{A0}(1 - X)$, Eqn (5) can be rewritten as:

$$X = \frac{kt}{1 + kt}$$

The kinetic model with $-r_{fA} = kC_A$ can also be verified by the data obtained from a CSTR if the plot of $\ln(-r_{fA})$ vs $\ln C_A$ gives a straight line, where $-r_{fA} = F_{A0}X/V$ is derived from Eqn (5).

If the reaction of RBr is of pseudo-first-order, then the conversion of RBr can be calculated by using Eqn (6) given that $\tau = V_{org}/v_{org, o}$ where $V_{org}$ is the effective reaction volume of the organic phase and $v_{org, o}$ is the inlet volumetric flow-rate of the organic solution.

3 RESULTS AND DISCUSSION

3.1 Immobilization reaction
In the preparation of triphase catalysts, the variables affecting the immobilization reaction, including the physical properties of the polymeric support (extent of chloromethylation, degree of crosslinking, particle size), temperature, kinds of organic solvent, and molar ratio of tri-$n$-butylamine to chloromethyl group in support, were investigated.

Based on the experimental results, the following conditions were adopted for preparing the catalysts used for the subsequent triphase catalytic experiments: (1) chloromethylated polystyrene with 200–400 mesh containing 2 mol% divinylbenzene and 4.3 meq of chloromethyl group per gram of dry particle was used as the polymeric support, (2) the immobilization temperature was about 70 $^\circ$C, (3) a polar aprotic compound (DMF) was used as an organic solvent, and (4) the molar ratio of tri-$n$-butylamine to chloromethyl group inside the support was about 6:1.

3.2 Triphase catalysis in the batch reactor
The kinetic study performed in the batch reactor allowed for the effects of agitation speed, ion-exchange capacity of catalyst, initial concentrations of NaOPh and RBr, catalyst loading, and reaction temperature on the conversion of $n$-butyl bromide to be investigated as well as for the determination of a proper operating condition for operating the continuous-flow stirred vessel reactor.

3.2.1 Mass transfer resistance
In a liquid–liquid–solid reaction system, the interfacial and intraparticle mass transfer may strongly affect the apparent reaction rate. However, when the organic and aqueous reactants are immiscible in the aqueous and organic phases, respectively, as in this study, the reaction will take place only on the exterior surface of the catalyst particles. Therefore, the intraparticle mass transfer was not considered in this study. As to the interfacial mass transfer, increasing the agitation speed might increase the contact area between, and the relative velocity of, liquid–liquid and liquid–solid phases, hence diminishing the interfacial mass transfer resistance. In the present system, the interfacial mass transfer resistance is negligible when the agitation speed is above 400 rpm. The agitation speed was fixed at 1000 rpm in the following experiments.

3.2.2 Ion-exchange capacities of catalysts
In general, increasing the extent of immobilization (ion-exchange capacity) of the catalyst increases both the amount of active sites in and the hydrophilicity of the catalyst, and thus facilitates the ion-exchange between the catalyst and OPh$^-$ in the aqueous phase as well as the reaction rate. However, a large increase in the hydrophilicity is not beneficial to the nucleophilic substitution of organic reactant. Therefore, catalysts with various levels of immobilization that affect the etherification of $n$-butyl bromide were examined. The catalyst with an ion-exchange capacity of 1.738 meq g$^{-1}$ was found to be suitable for the present reaction and was used in the remaining experiments.

3.2.3 Effect of initial NaOPh concentration, [NaOPh]$o$
Figure 2(a) reveals that the conversion of RBr was almost independent of the initial concentration of sodium phenolate, [NaOPh]$o$, in the earlier stage though some dependence emerged in the later stage when [NaOPh]$o$ was low (≤2.36 mol per dm$^3$ of aqueous phase) but was lower when [NaOPh]$o$ was high (≥3.08 mol dm$^{-3}$). Notably, at the lowest [NaOPh]$o$ (0.72 mol dm$^{-3}$), the reaction rate declined after 40 min because the amount of [NaOPh] left in the reactor was too low to furnish the ion-exchange reaction (NaOPh + QBr$^{−}$ $\rightarrow$ NaBr + QOPh$^-$). With [NaOPh]$o$ = 1.20 mol dm$^{-3}$, the same thing was seen after 90 min. With [NaOPh]$o$ greater than 2.36 mol dm$^{-3}$, the ionic strength of the aqueous phase was significantly increased and the water content on the external surface of the catalyst decreased, this happened because a larger amount of NaOPh in aqueous solution attracts a larger amount of water molecules. The hydrophilicity of the triphase catalyst
in the aqueous solution subsequently decreased, thereby reducing the capacity of $\text{OPh}^-$ to combine with the active center in the catalyst despite an excess amount of $\text{NaOPh}$. This explains how the conversion was lower when $[\text{NaOPh}]_0$ was greater.

3.2.4 Effect of initial $\text{RBr}$ concentration, $[\text{RBr}]_0$

The results shown in Fig 2(b) can be explained as follows. Similar to the reasoning in the above section, when the initial concentration of $\text{RBr}$ in the organic phase, $[\text{RBr}]_0$, was low ($\leq 0.72 \text{ mol dm}^{-3}$) compared with $[\text{NaOPh}]_0$, the conversion of $\text{RBr}$ was independent of $[\text{RBr}]_0$ throughout the whole course of the reaction. However, when $[\text{RBr}]_0$ was higher, its conversion was no longer independent of $[\text{RBr}]_0$—its conversion was lower because NaOPh becomes the limiting reagent, and because a high $[\text{RBr}]$ induces an increase in the lipophilicity of triphase catalysts. It is worth noting that $\text{RBr}$ has a higher polarity than the organic solvent toluene.

3.2.5 Catalyst loading

Figure 3 reveals the effect of adding a support on a bi-liquid-phase reaction system as well as that of catalyst loading on the triphase catalytic reaction system. The conversion of $\text{RBr}$ increased significantly when the catalyst loading was increased from 0 to 50 g per dm$^3$ of the liquid in reactor and showed a further slight increase when catalyst loading was increased from 50 to 70 g dm$^{-3}$. Moreover, the conversion was lower with the addition of support to the bi-liquid-phase reaction system. These phenomena might occur because of the following. The etherification reaction can proceed without catalyst, thereby, the rate of reaction is the sum of those of noncatalytic and catalytic reactions. When solid particles are added, the contact area between the two liquid phases is reduced, leading to a decrease in the noncatalytic reaction rate. In addition, when the catalyst loading is high, the chance of the reactant molecules being catalyzed by the catalyst particles is no longer proportional to the amount of catalyst. Consequently, the overall reaction rate does not increase noticeably at higher catalyst loading. Our results suggest that to obtain a high conversion and use catalyst most effectively, a suitable catalyst loading for this system is about 50 g dm$^{-3}$.

3.2.6 Temperature

Figure 4(a) shows that, as predicted, the reaction rate increased with the temperature. In practice, too high a temperature might cause the evaporation of organic solvent and the decomposition of catalyst. A suitable reaction temperature for this system should be in the range of 70–80°C; 70°C was chosen for the following experiments.

3.2.7 Rate expression and activation energy

We evaluated the rate expression and activation energy under optimal conditions. Because the relationship of $-\ln(1-X)$ and reaction time is linear, as shown in Fig 4(a), this triphase catalytic reaction can be represented by a pseudo-first-order model ($-\ln(1-X) = k[RBr]$) when the concentration of sodium phenolate (NaOPh) is in proper excess to that of RBr. The apparent activation energy and the pre-exponential factor were found to be 87.8 kJ mol$^{-1}$ and
3.6 × 10^{11} \text{ min}^{-1} \), respectively, from the Arrhenius plot (Fig 4(b)).

### 3.3 Triphase catalysis in a continuous-flow reactor

In the evaluation of the performance in the CFSVR, the effects on the reaction of inlet concentration of organic and aqueous reactants, the volumetric flow rate of organic and aqueous phases, and the stability of triphase catalyst were investigated. Furthermore, the apparent reaction rate constant was also determined from the CFSVR to compare with that obtained from the batch reaction system. The mixing model inside the CFSVR was evaluated by comparing the experimental conversion and the theoretical one.

#### 3.3.1 Inlet concentration of RBr, [RBr]

To explore its effect on the conversion of RBr, [RBr] was varied from 0.36 to 2.16 mol dm\(^{-3}\) while the inlet concentration of sodium phenolate (NaOPh) was fixed at 1.2 mol dm\(^{-3}\). Figure 5 indicates that conversion remains constant at first and then decreases markedly as [RBr] increases. This result can be explained by referring to results from the batch reactor. When [RBr] is low, say less than 0.72 mol dm\(^{-3}\), the average concentration of NaOPh in the reactor is in excess (about four times that of RBr). Under these conditions, the conversion of RBr is independent of [RBr]. However, when [RBr] is increased, the molar ratio of NaOPh to RBr in the reactor becomes smaller, and NaOPh becomes the limiting reagent, thereby conversion of RBr declines because there is not enough NaOPh to furnish the reaction.

#### 3.3.2 Inlet concentration of NaOPh, [NaOPh]

Figure 6 shows the effect of different [NaOPh] on the conversion of RBr with [RBr] fixed at 0.72 mol dm\(^{-3}\). Increasing [NaOPh] caused RBr conversion to increase to a maximum value and then decrease. The average [RBr] in the reactor was about 0.13–0.23 mol dm\(^{-3}\) while [NaOPh] varied from 0.21 to 4.3 mol dm\(^{-3}\). As mentioned above, when [NaOPh] was lower than 1.2, NaOPh in the reactor was not in large excess, hence the conversion of RBr was dependent on [NaOPh] and increased with increasing [NaOPh]. However, when [NaOPh] was higher than 2.4, the average [NaOPh] was greater than 1.8 mol dm\(^{-3}\). This caused an appreciable increase in the ionic strength in the aqueous phase, which restrained the ion-exchange between the catalyst and OPh\(^{-}\), resulting in the lower conversion seen. Notably, doubling [NaOPh] from 1.2 to 2.4 mol dm\(^{-3}\) only slightly enhanced the conversion. [NaOPh] should not exceed 1.2 mol dm\(^{-3}\) when [RBr] is 0.72 mol dm\(^{-3}\).

#### 3.3.3 Volumetric flow rate of organic and aqueous phases

It is well-known that the conversion will decrease with increasing the flow rate because of shorter space time (contact time), and it will not change when the flow rate is kept constant. In this study, the conversion of RBr did decrease as the flow rate of the organic phase was increased (Curves A and B in Fig 7). However, it only decreased moderately when the flow rate of organic phase was fixed and the flow rate of aqueous phase was increased (Curve C).

The decrease in the conversion of RBr with increasing the flow rate of aqueous phase when the flow rate of organic phase is fixed can be explained as the follows. When the flow rate of aqueous phase is increased, the concentration of NaOPh in the aqueous phase will decrease due to a shorter contact time. Therefore, the ionic strength of the aqueous phase, and
Synthesis of n-butyl phenyl ether

3.3.4 Stability of triphase catalyst

Figure 8 reveals the effect of on-stream-time on the conversion of RBr in the CFSVR. The conversion decreased from 76% to 60% after 27 h. This result is not beyond our expectation, because the deactivation of the triphase catalysts in batch reactors has been reported previously. As mentioned by Starks et al.,

10

the loss in catalytic activity may be attributed to the following three factors: (1) the catalyst is thermally decomposed via the Hofmann elimination and reverse Menshutkin reaction

11

(2) the structure of the catalyst is destroyed by the stirrer because its mechanical strength is poor and (3) the incorporation of impurities into the catalyst structure. Prior to the industrial applications, the stability of catalysts should be improved.

3.3.5 The mixing pattern inside the CFSVR

To understand the mixing mode inside the CFSVR, the predicted values of conversion for a CSTR were compared with the experimental value. The predicted X value for a CSTR at 70 °C with \( \tau = \frac{V_{\text{org}}}{v_{\text{org}}} = 100 \text{ cm}^3 / 0.5 \text{ cm}^3 \text{ min}^{-1} = 200 \text{ min} \) is obtained from Eqn (6), where the value of k is evaluated from the

center \((Q^+)\) in the catalyst. A similar explanation has been given in the above for discussing the effect of \([\text{NaOPh}]_0\) on the triphase catalysis in the batch reactor.

The small difference between Curves A and B may be explained by the same reasoning. Note that Curve A was obtained with a fixed flow rate of aqueous phase \((0.5 \text{ cm}^3 \text{ min}^{-1})\) while Curve B was with an increased flow rate of aqueous phase \((0.6–1.0 \text{ cm}^3 \text{ min}^{-1})\). The concentration of NaOPh in the latter case was slightly higher than that in the former case, thereby resulting in lower conversion of RBr.

in turn, the hydrophilicity of triphase catalyst in the aqueous solution, subsequently decreases, reducing the capacity of OPh\(^-\) to combine with the active
Batch operation:

\[
X = \frac{kt}{1 + kt} = \frac{0.0165 \times 200}{1 + 0.0165 \times 200} = 0.767
\]

However, as shown in Fig 6, the experimental value of conversion for CFSVR under the same conditions is 0.821. It is well-known that conversion in a CSTR is less than that in a batch reactor. Here, the conversion in the CFSVR (0.821) was greater than the predicted value for a CSTR (0.767), but lower than that in a batch reactor (0.963). This difference demonstrates that the mixing pattern inside the CFSVR is dissimilar to a perfectly mixed CSTR. In fact, the organic and aqueous solutions in the reactor are segregated. The organic droplets are suspended in the aqueous phase or vice versa, additionally the catalyst particles and the dispersed phase are not well mixed, thereby the experimental conversion is higher than the predicted value.

4 CONCLUSIONS

To evaluate the feasibility of using a continuous-flow stirred vessel reactor (CFSVR) for triphase catalysis, the etherification of \(n\)-butyl bromide and sodium phenolate catalyzed by a polystyrene-supported phase-transfer catalyst was used as a model reaction. The experimental results of a kinetic study with a batch reactor indicated that the catalysts prepared had good catalytic activity for the reaction. The etherification reaction can be represented by a pseudo-first-order kinetic model, \(-r_{RB} = k[RBr]\), when the concentration of NaOPh is in proper excess to that of RBr, and the apparent activation energy is 87.8 kJ mol\(^{-1}\).

The results of this preliminary investigation suggest that CFSVR used for triphase catalysis provides a feasible means of reusing catalysts with a continuous-flow reactor which may be employed for industrial applications. However, the stability of the catalysts should be improved. The use of coupling reagents having a better binding ability with active species and supports with a higher mechanical strength are two feasible ways to achieve this. Besides, the use of a magnetic stirrer with ultrasonic mixer might reduce the destruction of triphase catalysts. Extensive work on these subjects is now in progress in our laboratory. Parts of the results will be released soon. Further research on the CFSVR, including the improvement of catalyst properties and the performance of the reactor, is encouraged.

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