Catalytic Kinetics of Quaternary Ammonium Poly(styrene-*co*-methylstyrene) Resin

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*The catalytic kinetics and synthesis of poly(styrene-*co*-chloromethylstyrene) resin of different degrees of crosslinkages and ring substitutions were investigated by copolymerizing styrene and chloromethylstyrene through crosslinking with divinylbenzene. Poly(styrene-*co*-chloromethylstyrene) quaternary ammonium salt was obtained with activating poly(styrene-*co*-chloromethylstyrene) resin with tertiary amine. More than 20 types of poly(styrene-*co*-chloromethylstyrene) quaternary ammonium catalyst were prepared, with reaction conditions including immobilized time (0.125~4 days), concentration of tertiary amine (0.1~2 kmol/m^3), kinds of solvents in immobilization (methanol, ethyl alcohol, and DMF), and kinds of tertiary amines (trimethylamine, triethylamine, tripropylamine, tri-*n*-butylamine, tri-*n*-pentylamine, tri-*n*-hexylamine, and tri-*n*-octylamine). These catalysts were used to achieve the optimum allylation of phenol. The reactions were conducted and studied individually with either equal mole or equal weight of catalyst. The best reactivity for the allylation of phenol was obtained when the structure of the quaternary ammonium catalyst was 10% degree of ring substitution and 2% degree of crosslinkage activating with trihexylamine. The turnover number and the effectiveness factor were also calculated.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2535–2544, 2006
Keywords: reaction kinetics, phase-transfer catalysis, triphase, turnover number

Introduction

Liquid-liquid phase-transfer catalysis (PTC) is an effective tool for synthesizing organic chemicals from two immiscible reactants.[1-3] Currently most PTC reactions are carried out on an industrial scale in the batch mode in mixer-settler arrangements. However, the process of using a two-phase phase-transfer catalytic reaction always encounters the problem of separation and purifying the final product from the catalyst. Although the catalyst can be separated from the product by distillation or extraction, the operating cost is increased and the purity of the product is reduced.

Poly(styrene-*co*-chloromethylstyrene) crosslinked with divinylbenzene, which is immobilized with quaternary ammonium salts, has been investigated to synthesize fine chemicals,[1-11] and it was found that the microenvironment of the polymer support played a crucial role in enhancing the reaction rate. Now, more information about characterization of the polymer structure, the interaction among organic solvent, resin, and aqueous solution, and the reuse of the catalyst is required to facilitate application. The polymer structure was almost used with different degrees of ring substitution and crosslinkage, as well as pore size in the interior of the pellet. These previous experimental results are clearly of use. However, the distribution of the active site (quaternary ammonium salt) in the interior of the pellet and the reactivity of the active site for activating with different kinds of tertiary amines have received little attention. Another, in a solid-liquid reaction, the diffusion is the main problem in improving the reaction rate. In a triphase catalysis, the structure of the catalyst is made from a hydrophilic quaternary ammonium group and hydrophobic polymer-supported poly(chloromethylstyrene-*co*-styrene) with crosslinking with divinylben-

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zene. Thus, the hydrophilic quaternary ammonium group is an active site. Furthermore, the reaction was conducted in an organic and aqueous solution. However, the diffusion issue in a triphase reaction has rarely been discussed. Hence, this article aims to understand the diffusion problem of reactant and the reactivity of the active site within the triphase catalyst by comparing the two-phase catalyst, and design different structures with different distributions of the active site in the interior of the catalyst in order to achieve the optimum structure (or microenvironment) of the catalyst.

Experimental Section

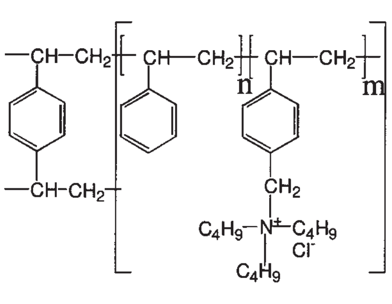
Materials

Allyl bromide (Fluka, 99.5%), chloromethylstyrene (Aldrich, 97%), divinylbenzene (Aldrich, 80%), phenol (R.D.H., 99%), styrene (R.D.H., 99%), trimethylamine (R.D.H., 98%), triethylamine (R.D.H., 98%), tripropylamine (Aldrich, 98%), tri-*n*-butylamine (Aldrich, 98%), tri-*n*-pentylamine (Aldrich, 98%), tri-*n*-hexylamine (Aldrich, 96%), tri-*n*-octylamine (Aldrich, 98%), and other reagents are all expanded chemicals.

Preparation of triphase catalyst

The synthetic procedure for polymer-supported phase-transfer catalysis (triphase catalysis) was identical to that of Wu and Lee.[10] The typical compositions of styrene, chloromethylstyrene, and divinylbenzene (crosslinkage agent) in the resin were 76 mol %, 20 mol%, and 4 mol%, respectively. Chloromethylstyrene was introduced into the polymerization reactor at a selected time interval. The particle sizes of the polymer pellet were determined by sieve analysis. Weight percents of microporous polymer collected were 25-35 mesh = 10%, 35-45 mesh = 20%, 45-60 mesh = 33%, 60-80 mesh = 20%, and 80-200 mesh = 17%.

5.0 g of polymer pellet, 100 cm^3 of methanol, and 1 $kmol/m^3$ of tertiary amine were introduced into a 250 cm^3 flask at 60°C. The reaction mixture was shaken (100 rpm) for 1 day. After reaction, the polymer was then filtered and washed with methanol, acetone, and anhydrous methanol, and dried under vacuum at 60°C. The molecular structure of polymer-supported (styrene-chloromethylstyrene-divinylbenzene) resin is expressed as



Characterization of resins

The procedure for determining imbibed solvent composition of the resin is identical to that in Wang and Wu.[4] Here, a 125 cm^3 funnel equipped with a fritted disk served as the testing apparatus. Known quantities of the catalyst pellet, organic solvent, and alkaline solution were added to the funnel, and the external liquid phase was then removed from the slurry using an aspirator. The wetted resin was placed in a flask containing 15 cm^3 of i-propanol from the catalyst pellets. The amounts of solvent and water in i-propanol were measured by HPLC and potentiometer (Karl Fischer Titration, Mettler Toledo DL38), respectively.

Volume ratios (V_R = (vol. of wet swollen resin/vol. of dry resin) = $[\Sigma_i\ (m_{si}/\rho_{si}) + (m_P/\rho_p)/(m_P/\rho_p)]$) were calculated by assuming that the polymer density ρ_p was 1060 kg/m^3 (versus 1040-1065 kg/m^3 for amorphous polystyrene) and the densities of the solvents ρ_{si} and polymer in the resin were the same as those of pure solvent and pure polymer. In addition, m_p and m_{si} denote the mass of polymer and solvent, respectively, in the resin. Direct measurement of the porosity of the wetted swollen resin was very difficult because of the solvent within the pores. The measuring procedure of the porosity of the catalyst was identical to that of Wu and Lee.[10]

Kinetics of the triphase catalytic reaction

Next, 50 cm^3 of dichloroethane, 0.5 mmol of polystyrene-supported quaternary ammonium salt catalyst, allylbromide (0.61g, 0.005 mol), and diphenyl ether (0.11g) were added into a 250 cm^3 three-necked flask. After 10 min to allow the catalyst to swell, phenol (0.81g, 0.0086 mol) and sodium hydroxide (0.8g, 0.02 mol) with water (50 cm^3) were introduced into the flask. The reaction was conducted at 40°C under agitation rate of 400 rpm. For a kinetic run, aliquot samples were withdrawn from the reaction solution at selected time intervals. The sample (0.2 cm^3) was immediately added to the solution (0.5 cm^3 dichloromethane/0.5 cm^3 of diluted hydrochloric acid) to quench the reaction. The organic phase content was then quantitatively analyzed by HPLC using the method of internal standard.

Characterization property of quaternary ammonium poly(styrene-co-methylstyrene) catalyst

Ion-exchange capacity of the catalyst was determined by the Volhard method. First, the catalyst (0.5 g) and methanol (5 cm^3) were added into the flask. After 30 min to allow the catalyst to swell, HNO_3 (0.2 cm^3, 0.05 $kmol/m^3$) was added to the flask. After 2 h, the catalyst was filtrated and washed by deionized water (50 cm^3). Then, ammonium iron III solution (2 cm^3, 0.015 $kmol/m^3$) was added into the solution, which turned yellow. KSCN (0.2 cm^3, 0.02 $kmol/m^3$) was then added into the solution, which turned orange. The solution was titrated with $AgNO_3$ (0.015 N) until it was clear, and then $AgNO_3$ was added in excess (solution was green-yellow). The white solid was separated by filtration. The solution was heated until suspended substances formed, and then cooled. It was then titrated with KSCN (0.02 $kmol/cm^3$) until the solution color changed from yellow to orange.

Mathematical Modeling of Reaction Kinetics

The allylphenyl ether was formed from the reaction of sodium phenolate reacting with allylbromide using anion-exchange resin as a triphase catalyst. The reaction equation is

$$C_3H_5Br_{(o)} + C_6H_5OH_{(a)} + NaOH_{(a)} \xrightarrow{\text{triphase catalyst}} C_6H_5OC_3H_{5(o)} + NaBr_{(a)} + H_2O_{(a)}. \quad (1)$$

The reaction was carried out in a three-phase liquid (organic) – solid (catalyst) – liquid (aqueous) condition. In general, the reaction mechanism of the triphase catalysis is: (i) mass transfer of reactants from the bulk solution to the surface of the catalyst pellet, (ii) diffusion of reactants to the interior of the catalyst pellet (active sites) through pores, and (iii) surface or intrinsic reaction of reactants with active sites. The substitution reaction in the organic phase and ion exchange reaction in the aqueous phase occurred. The reaction expression for the formation of allylphenyl ether is:

$$r = \frac{dY}{dt} = \eta k C_{AS} \cdot \frac{w \times [Cl^-]}{V \times 10^6} \quad (2)$$

where r is a formation rate of allylphenylether, Y is the yield of allylphenylether, η is an effectiveness factor, k is the reaction-rate constant, C_{As} is the concentration at the surface of the pellet, w is the weight of the catalyst, $[Cl^-]$ is the chloride density of the catalyst (active site), and V is the solvent volume.

The amount of the catalyst introduced into the reaction system was different with the different chloride densities of the resins. For example, based on the equal mole of the catalyst conducted in the reaction system, a smaller chloride density of the catalyst would correspond to a larger amount of catalyst introduced into the reaction system. However, the incremental amount of catalyst increases the catalyst surface area, and also increases the reaction rate. Hence, the following discussion is separated into two cases for the reaction: equal mole of catalyst and equal weight of catalyst.

(a) Equal mole of catalyst used in the reaction

If the catalyst was used as an equal mole condition in the reaction system, Eq. 1 can be rewritten as follows:

$$\frac{r}{a} = \frac{\eta}{a} \cdot k \cdot C_{AS} \cdot \frac{w \times [Cl^-]}{V \times 10^6} \quad (3)$$

where a is a wetted surface area of the catalyst. The value of ($w \times [Cl^-]/V$) is constant, that is, the concentration of the active site remained constant in the kinetic discussion. Eq. 1 was divided by the surface area of the catalyst to eliminate the effect of the amount of the catalyst because the incremental amount of catalyst increased the reaction rate when the molar amount of the catalyst used was kept constant.

The definition of the wetted surface area of the catalyst calculated is given as:

$$a = V_R^{2/3} \cdot a' \cdot w \quad (4)$$

where V_R denotes a volume ratio of wetted catalyst to dry catalyst and a' denotes the surface area per dry catalyst. The dry surface area of the catalyst for RS 20% and CL 4% observed was during 1.2-1.6 m^2/g for different synthesizing methods by the BET method. So the average surface area a' was used to calculate with 1.4 m^2/g in this study. The average volume ratio of the catalyst was found to be around 1.86 by means of analyzing the imbibed composition of the catalyst. Substituting Eq. 4 into Eq. 3, Eq. 3 can be rewritten as:

$$\frac{r}{a} = \eta \cdot k \cdot C_{AS} \cdot \frac{[Cl^-]}{V_R^{2/3} a' V \times 10^6}. \quad (5)$$

(b) Equal weight of catalyst used in the reaction

If the catalyst was used as an equal weight condition in the reaction system, Eq. 1 could be rewritten as:

$$\frac{r}{[Cl^-]} = \eta k C_{AS} \frac{w}{V \times 10^6}. \quad (6)$$

In a heterogeneous catalytic reaction,[12] the catalytic effectiveness η for a second-order reaction within a spherical catalyst at steady state in a fluid-solid system is:

$$\eta = \frac{3\phi \coth(3\phi) - 1}{3\phi^2}, \quad (7)$$

and the Thiele modulus ϕ_i^s and effective diffusivity are:

$$\phi = \frac{R_{avg,wet}}{3} \sqrt{\frac{k\left(\frac{w[Cl^-]}{V}\right)}{D_e \times 10^6}} \quad (8)$$

and

$$D_e = \frac{\varepsilon}{\tau} D, \quad (9)$$

respectively, where D and D_e are the bulk diffusivity and effective diffusivity, respectively, within the catalytic particle, which can be calculated by using the Hayduk and Minhas correlation[13]; $R_{avg,\ wet}$ is the wetted catalyst radius; and ε and τ are porosity and tortuosity, respectively.

Results and Discussion

In previous studies,[14-16] the formation kinetics of allyl phenyl ether using tetra-*n*-butyl ammonium bromide (TBAB) or quaternary ammonium poly(styrene-*co*-chloromethylstyrene) resin as a phase-transfer catalyst were studied in an organic solvent/alkaline solution. Since this article studies the microstructure effect of quaternary ammonium poly(styrene-*co*-chloromethylstyrene) resin as triphase catalysis for the reaction, the reaction system chosen for study was also the reaction of allyl bromide with phenol. The reaction mechanism of the triphase reaction was presented in our previous work (Figure 1).[9]

The agitation rate was also an important factor in the reaction. Generally speaking, the yield of reaction increases with the agitation rate in a liquid-liquid phase-transfer catalytic reaction. The interfacial surface area and mass transfer between two phases were increased with increasing agitation rate, and that would increase the yield of the reaction. In this study, the

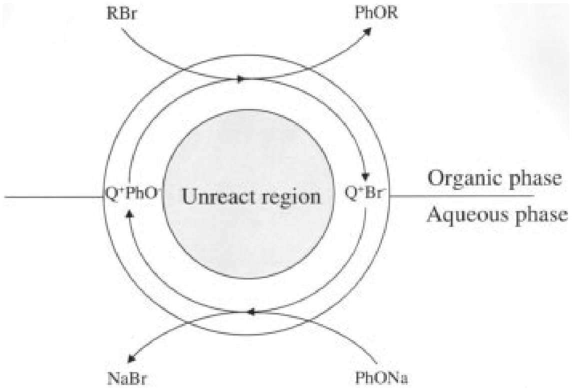


Figure 1. Reaction mechanism of the polymer-supported triphase reaction.

reaction rate remained nearly constant when the agitation rate was more than 200 rpm. Therefore, the agitation rate was set at 400 rpm in the following discussion.

In general, the polymer-supported catalyst has a spherical shape. The catalyst particle size will directly influence the exchange velocity, separation, layer pressure drop, and swelling. When a process has an ion-exchange reaction, the particle size should be small and uniform, and 20~50μm is usually used. Although a smaller catalyst can increase the reaction rate, the flow resistance of the solution and volume swelling of the catalyst are increased in industrial processes. These disadvantages increase the operation and equipment charges. In this study, a larger catalyst particle size of 45-60 mesh was chosen, with average diameter of 0.302 mm.

The single pore volume will influence the imbibed composition of the solvent and reactant. It also influences the immobilized amount of the active site in an immobilization reaction. In this study, the pore volume and surface area of the catalysts measured by the BET method were in the range of 0.0044~0.0085 cm^3/g and 1.2~1.6m^2/g, respectively. The pore volume, average surface area, and pore size of the dry catalyst were 0.0067cm^3/g, 1.44m^2/g, and 61 Å, respectively.

Effect of added times of CMS in synthesis of polymer-supported resin

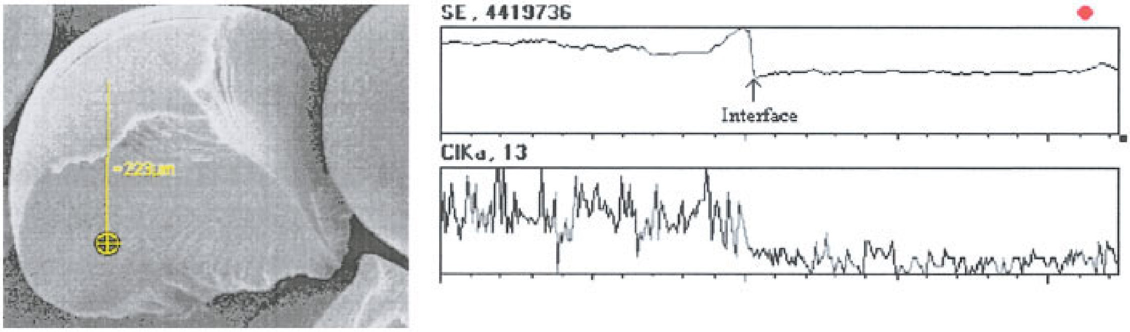
In a solid-liquid reaction, the diffusion is mainly the problem for improving the reaction rate. In a triphase catalysis, the catalyst composition can be separated to the hydrophilic quaternary ammonium group and hydrophobic polymer-supported poly(chloromethylstyrene-*co*-styrene) with crosslinking with divinylbenzene. Therefore, the optimum reactivity of this triphase reaction is more complex than that of the traditional solid-fluid system. Ruckensten and Hong reported that crosslinked polystyrene latexes with surface-bound quaternary ammonium groups have been prepared so that the functional monomer chloromethyl styrene was introduced into a partially polymerized concentrated emulsion of styrene and divinylbenzene in a polymerization.[17] They also reported that the activity and selectivity of the meldrum acid increased when the partial polymerization time increased. In addition, if the active site of the quaternary ammonium group is immobilized too close to the central part of the catalyst to increase the diffusion resistance and hydrophobic steric resistance, the reaction rate was dramatically decreased. On the other hand, all quaternary ammonium groups were bounded on the surface of the catalyst so as to reduce the amount of active sites and the reactive surface area. Hence, setting up a good microenvironment for the triphase catalysis plays a crucial role in enhancing the reaction rate. In this study, Ruckensten and Hong's method was first conducted to prepare this triphase reaction system. Binding active sites on the surface zone of the catalysts since the substitution reaction was conducted in the surface zone of the catalysts. Hence, the designed catalysts of this study were synthesized by changing the length of time that chloromethyl styrene (CMS) was added into the copolymerization reaction after styrene and divinylbenzene had been added.

The morphology of the catalyst synthesized by different added times of chloromethylstyrene in the polymerization was observed by scanning electron microscopy (SEM). SEM analyzes electrons that are scattered from the sample's surface and monitors the morphological observation of the polymer resin. The elemental analysis is determined by means of energy dispersive X-ray spectrometer (EDS) methods. Figure 2 shows the EDS mapping values of the Cl element for added times of CMS of 0.5, 1, and 1.5 h, respectively. The SEM pictures show that their surface morphologies and EDS mapping of the Cl element were different from each other. The smoothing degree of the surface of the polymer particle was reduced with increasing either a longer time for adding the CMS or the concentration of CMS. The surface compositions of the catalyst were determined by EDS. The bound chloromethyl group within the surface region related to the internal region of the functionalized polymer particles increased with increasing the longer time for adding CMS. It is demonstrated that the more chloromethyl group (that is, active site) was successfully bound to the surface region of the catalyst.

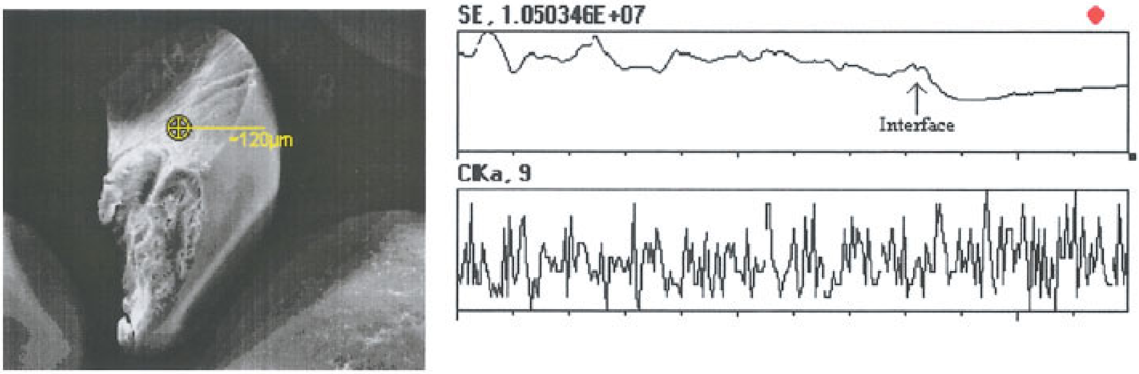
Figure 3 shows the effect of different lengths of time for the addition of CMS to synthesize the catalyst for the yield of PhOR. The increment of added time of CMS did not increase the yield of the reaction. According to the experimental result in Figure 3b, the reactivity of this allylation of phenol is decreased with increasing length of time for adding CMS because the hydrophilicity in the surface region of the active site increases when the concentration of the catalyst increases. This finding differs from the results of Ruckensten and Hong.[17] Furthermore, the chloride density of the catalyst was reduced when the added time for CMS increased, as shown in the caption for Figure 3. This is because the chloride density of the catalyst is too low on the surface region to obtain a higher reaction rate. Therefore, the bound active site on the surface of the catalyst in a triphase reaction is not a good application for industrial processes.

Effect of immobilization time with tri-n-butyl amine in resin

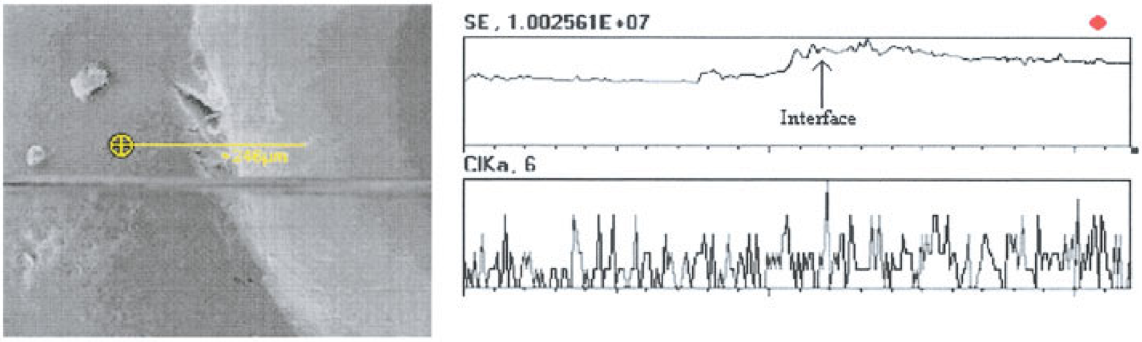
The reactivity of phenol allylation could not obtain a higher PhOR yield with different structures of polymer pellets and different added times for CMS, as mentioned above. However, the reactivity of allylation of phenol could be increased with decreasing immobilization time due to tri-*n*-butyl amine of 1



(a) For 0.5h added chloromethylstyrene



(b) For 1h added chloromethylstyrene



(c) For 1.5h added chloromethylstyrene

Figure 2. EDS mapping value of Cl element.

Resin (RS 20%, CL 4%) was prepared by adding chloromethylstyrene at the reaction times: (a) 0.5 h, (b) 1h, and (c)1.5 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

kmol/m^3 within the polymer pellet having the same structure of polymer-supported resin of RS 20% and CL 4%, as shown in Figure 4. The catalyst was introduced into the reaction system in the case of equal mole and equal weight. The chloride density in the catalyst was gradually increased up to the immobilization time of one day, and then remained almost the same, as shown in the caption to Figure 4. According to Eqs. 5 and 6, the yields of PhOR in Figures 4b and 4d were divided by the wetted surface area and chloride density per catalyst, respectively. The trend of the yield of allylation of phenol in Figure 4a is the same as those in Figures 4b and 4d, and different from that in Figure 4c. It is demonstrated that the lower active site density in the resin could give a higher reactivity of allylation of phenol (Figures 4b and 4d), that is, the reactive microenvironment in the resin with lower active site density was good. This finding corresponds to the result of previous studies, which found that the solvating capability between quaternary salt and water could reduce the quaternary salt's reactivity in the organic phase in a phase-transfer-catalyzed reaction.[18,19] Thus, too much water content in the interior

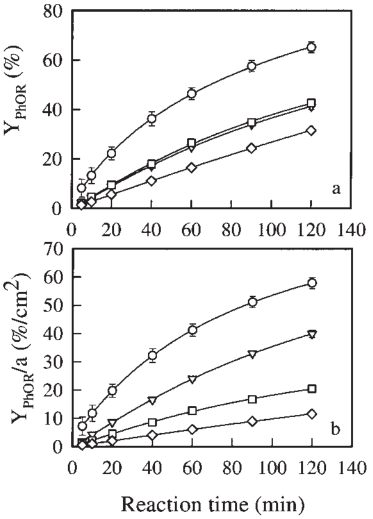


Figure 3. Effect of added time of chloromethylstyrene in synthesis of catalysts for PhOR yield.

Resin (RS 20%, CL 4%) = 0.5 mmol, 40°C, 400 rpm, aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm^3: C_3H_5Br = 0.005 mol, added time and [Cl^-] = (○) 0h, 0.942 mmol/g; (▽) 0.5 h, 1.03 mmol/g; (□) 1h, 0.509 mmol/g; (◇) 1.5 h, 0.389 mmol/g.

of the catalyst would reduce the reactivity of the allylation of phenol.

Effect of tri-n-butylamine concentrations in immobilization

Figure 5 shows the effect on the yield of PhOR due to tri-*n*-butylamine concentration at the immobilization time of 6 h in the methanol solution. The catalyst was introduced into the reaction system in the case of equal mole and equal weight. The immobilization experiment would prepare the lower chloride density of the catalyst having the same structure. The chloride density of the catalyst was increased with increasing tri-*n*-butylamine concentration up to 1 kmol/m^3 in the immobilization. For equal mole of the catalyst in Figure 5a, the yield of PhOR increased with decreasing tri-*n*-butylamine concentration. The immobilized tributylamine concentration of 0.2 kmol/m^3 obtained was the best for this reaction because this catalyst can be used in more amount in the reaction, that is, more surface area, more than other catalysts. In Figure 5b, the yields of PhOR per surface area were increased with increasing tri-*n*-butylamine concentration. In the stirred triphase reaction, the mechanic system usually sprays out the catalysts on the wall of the reactor, so some catalysts would not contact the solution and reacted with the reactant. Hence, most catalysts conducted in the higher agitation may actually obtain lower reactivity (Figure 5b).

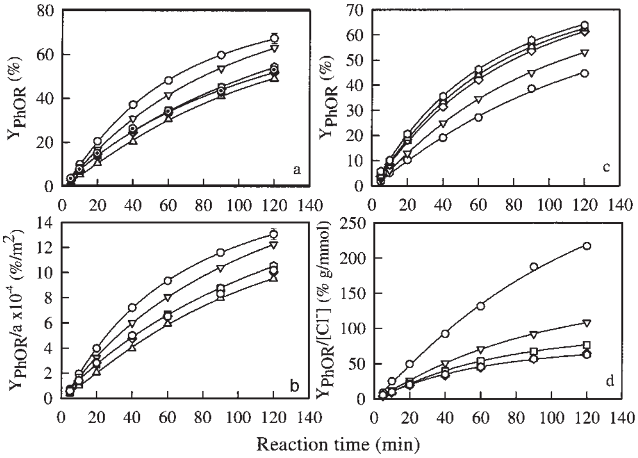


Figure 4. Effect of immobilized times with tri-*n*-butyl amine for PhOR yield.

(a,b): 0.5 mmol and (c,d): 1g of resin (RS 20%, CL 4%), 40°C, 400 rpm, aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm^3: C_3H_5Br = 0.005 mol, Immobilized time and [Cl^-] = (○) 3 h, 0.206 mmol/g; (▽) 6h, 0.490 mmol/g; (□) 12 h, 0.825 mmol/g; (◇) 1 day, 0.945 mmol/g; (△) 2 days, 0.978 mmol/g; (○) 3 days, 1.02 mmol/g; (⊙) 4 days, 1.03 mmol/g.

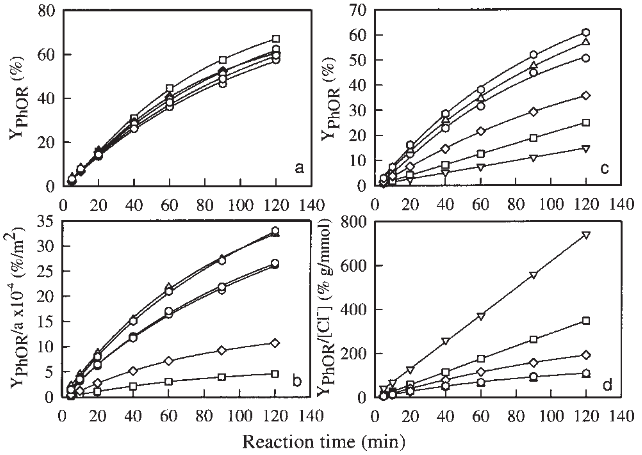


Figure 5. Effect of tri-*n*-butylamine concentration in immobilization for PhOR yield.

(a,b): 0.5 mmol and (c,d): 1g of resin (RS 20%, CL 4%), 40°C, 400 rpm; aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm^3: 0.005 mol of C_3H_5Br. Immobilization volume, tri-*n*-butylamine concentration, and [Cl^-] = (▽) 100 cm^3 of 0.1 kmol/m^3, 0.020 mmol/g; (□) 100 cm^3 of 0.2 kmol/m^3, 0.072 mmol/g; (◇) 100 cm^3 of 0.5 kmol/m^3, 0.187 mmol/g; (△) 100 cm^3 of 1 kmol/m^3, 0.566 mmol/g; (○) 100 cm^3 of 2 kmol/m^3, 0.562 mmol/g; (○) 200 cm^3 of 1 kmol/m^3, 0.483 mmol/g; (⊙) 50 cm^3 of 1 kmol/m^3, 0.472 mmol/g.

For the equal weight of the catalyst in Figure 5c, the higher tri-*n*-butylamine concentration had better effect on the reaction rate because the catalyst had higher chloride density (active site). In Figure 5d, the trend of yield of PhOR for tri-*n*-butylamine concentration was 0.1 kmol/m^3 > 0.2 kmol/m^3 > 0.5 kmol/m^3> 1 kmol/m^3 = 2 kmol/m^3. This finding corresponds to the result mentioned above, that the lower chloride density of the catalyst had the better reactivity of allylation.

In general, the reaction rate is increased with increasing the amount of catalyst used in the triphase reaction because the incremental amount of the catalyst increases the chloride density (that is, active site). However, many triphase reactions have been shown where the reaction rate was not directly proportional with the amount of catalyst. Using more catalyst for the reaction would only spray out more catalyst to the wall of the reactor. What amount of the catalyst is the best in the PTC reaction? The amount of the catalyst of 0.3∼1 g was the best range in this reactor geometry. Hence, the tri-*n*-butylamine of 1 kmol/m^3 is suggested as having the best efficiency for immobilization in engineering, so the tri-*n*-butylamine concentration of 1 kmol/m^3 was used as the standard immobilization concentration in the discussion below.

Effect of kinds of tertiary amines on immobilization

In the past, the triphase catalyst found to give the highest reactivity of the active site was the polymer-supported resin with activating with tri-*n*-butylamine. However, Lo reported that the polymer-supported resin with activating with tri-*n*-hexyllamine, not tri-*n*-butylamine, had the best reactivity of allylation of phenol by the combinatorial chemistry method.[20] However, he did not completely present and discuss the effect of different kinds of tertiary amines on the reaction. Hence, the current study used seven tertiary amines (trimethylamine, triethylamine, tripropylamine, tri-*n*-butylamine, tri-*n*-pentylamine, tri-*n*-hexylamine, and tri-*n*-octylamine) to activate the polymer-supported resin to evaluate their allylation reactivity in this study. Three immobilization solvents (methanol, ethanol, and DMF) were used to swell the catalyst to activate with the tertiary amine. DMF is more hydrophobic than other alcohols, and so could be used to immobilize the long carbon chain of the tertiary amine. The sequence of chloride density of catalyst for the solvent used in the immobilization of one day was methanol > ethanol > DMF, except for trioctylamine. Since the trioctylamine was so hydrophobic that it was not easily dissolvable in methanol, only the trioctylamine was put with DMF in the immobilization reaction. The order of magnitude for chloride density of the catalyst for the tertiary amine immobilized was trimethylamine > triethylamine > tripropylamine > tri-*n*-butylamine > tri-*n*-pentylamine > tri-*n*-hexylamine > tri-*n*-octylamine, as shown in the caption of Figure 6.

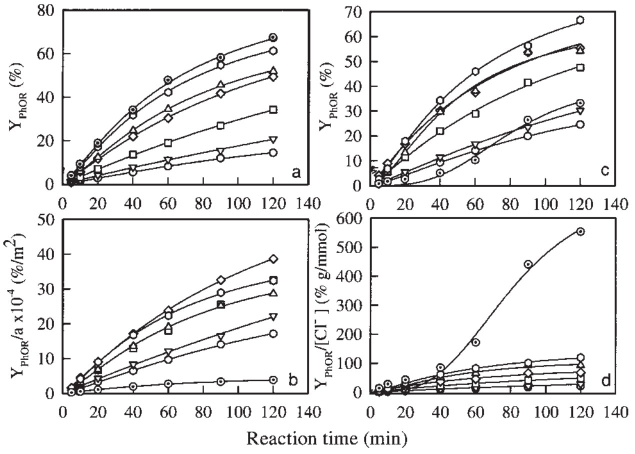


Figure 6. Effect of kinds of tertiary amines in immobilization for PhOR yield.

(a,b): 0.5 mmol and (c,d) 1g of resin (RS 20%, CL 4%), 40°C, 400 rpm; aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm^3: 0.005 mol of C_3H_5Br, immobilized 1 day in methanol; tertiary amine and [Cl$^-$] = (○) trimethylamine, 1.27 mmol/g; (▽) triethylamine, 1.138 mmol/g; (□) tripropylamine, 1.01 mmol/g; (◇) tributylamine, 0.830 mmol/g; (△) tripentylamine, 0.585 mmol/g; (○) trihexylamine, 0.560 mmol/g; (⊙) trioctylamine in DMF, 0.060 mmol/g.

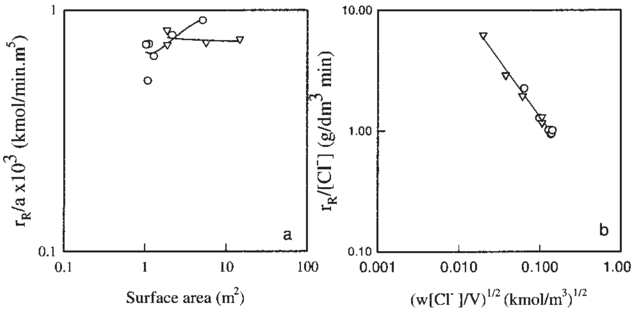


Figure 7. Effect of (a) surface area and (b) chloride density of the catalyst for reaction rate of allylation.

(○) Calculated from Figure 4, (▽) calculated from Figure 5.

Figure 6 shows the effect of the tertiary amine on the yield of PhOR using the catalyst of RS20%, CL4%. In Figure 6a, the sequence of the yield of PhOR for the tertiary amine was tri-*n*-octylamine > tri-*n*-hexylamine > tri-*n*-pentylamine > tri-*n*-butylamine > tripropylamine > triethylamine > trimethylamine. Figure 6b shows that the yield for PhOR using polymer-supported resin with tri-*n*-butylamine was better than those with tri-*n*-hexylamine or tri-*n*-pentylamine after reaction of 2 h. This result may have been because this catalyst used more amount, that is, more surface area, than the other catalysts.

The sequence of the yield of PhOR for tertiary amine was trihexylamine, tripentylamine, and tri-*n*-butylamine > tripropylamine > tri-*n*-octylamine, triethylamine > trimethylamine (Figure 6c). In Figure 6d, the order of magnitude for the reactivity of the allylation of phenol was tri-*n*-octylamine > tri-*n*-hexylamine > tri-*n*-pentylamine > tri-*n*-butylamine > tripropylamine > triethylamine > trimethylamine. The reactivity of the allylation of phenol was increased with increasing lipophilicity of the tertiary amine. Tri-*n*-octylamine was the best tertiary amine for reactivity of allylation of phenol, but this compound cannot easily be applied in industry because it has a lower chloride density in the catalyst (0.06 mmol/g), which makes it very difficult to immobilize on the catalyst. This finding demonstrates that the earlier conclusion that the polymer-supported resin activating with tri-*n*-butylamine is the best triphase catalyst, is wrong.

Effectiveness factor in the catalyst pellet

In general, the reaction mechanism of the classical fluid-solid reaction has the intra- and inter-particle diffusion problems. Liquid-solid-liquid triphase catalysis is more complicated than the traditional heterogeneous catalysis because it involves not merely the diffusion of a single gaseous or liquid phase into the solid catalyst. Both organic reactant and aqueous reactant exist within the pores of the polymer pellet. This study investigates how the reaction was influenced by pore diffusion. So, in order to obtain the results mentioned above, we calculate the effectiveness of the catalyst by the reaction rate to discuss the diffusion problem.

Figure 7 shows the relationships between (a) the initial reaction rate per wetted surface area and wetted surface area of the resin, and (b) the initial reaction rate per chloride density

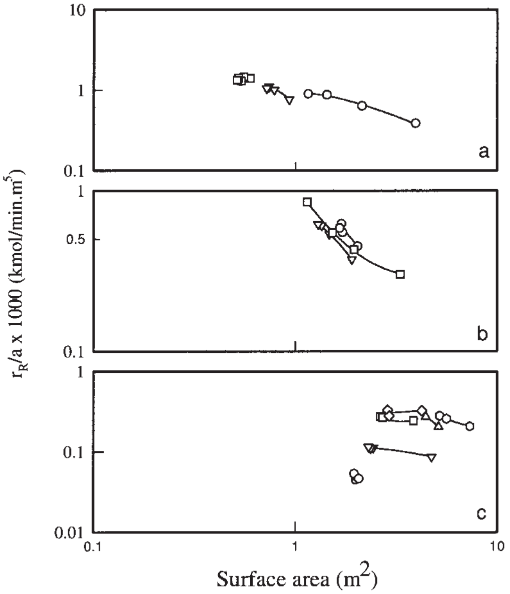


Figure 8. Effect of (a) degree of ring-substitutions ((○) RS 10%, (▽)RS 20%, (□) RS 40%); (b) degree of crosslinkage ((○) CL 2%, (▽) CL 4%, (□) CL 6%); and (c) kind of tertiary amines ((○) trimethylamine, (▽) triethylamine, (□) tripropylamine, (◇) tributylamine, (△) tripentylamine, (○) trihexylamine) for reaction rate of allylation of phenol on surface area of the catalyst.

Resin 0.5 mmol, 40°C, 400 rpm; aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm^3: 0.005 mol of C_3H_5Br.

and chloride density. The initial formation rate of product r_R was obtained by using the concept of the initial rate method, thereby restricting the content of allyl phenyl ether in the aqueous phase to less than 15%.[16] According to Figure 7a and Eq. 5, the initial reaction rate per wetted surface area was almost constant and independent of the resin surface area when the structure of the resin was the same for different immobilized types of tertiary amines. Figure 7b shows that the yield of PhOR per chloride density decreased with increasing chloride density of the catalyst. According to Figure 7b and Eqs. 7 and 8, the effectiveness factor was affected by the chloride density of the catalyst.

However, the value of the effectiveness factor was different with the different structures of the catalysts. Figures 8a and 8b show plots of the initial reaction rate per surface area of the catalyst on the surface area of the catalyst for different degrees of ring substitution and crosslinkage, respectively. This finding clearly demonstrates that the effectiveness factor was decreased with increasing degree of crosslinkage and decreasing degree of ring-substitutions, which were controlled by intraparticle diffusion. Figure 8c shows a plot of the yield of PhOR on different tertiary amines for immobilization. The sequence of the effectiveness factor for tertiary amine was tributylamine > trihexylamine, tripentylamine, and tripropylamine > triethylamine > trimethylamine. Because the polymer-supported resin with activating trimethylamine is hydrophilic, and the chloride density in the catalyst was high so as to imbibe more water within the catalyst, the reactivity was low.

According to Eq. 5, the effectiveness factor was assumed to be equal to one when the chloride density was 0.046 mmol/g (Figure 7b), and the intrinsic reaction-rate constant of this triphase allylation reaction using polymer-supported resin with tri-*n*-butylamine as a catalyst calculated was 3.1 (min·kmol/m^3)$^{-1}$ at 40ºC. Next, substitute the intrinsic reaction-rate constant into Eq. 8 to calculate the Thiele module, and then calculate the effectiveness factor by Eq. 7. The Thiele module and the effectiveness factor calculated were 0.03 and 1, respectively. Therefore, two effectivenesses are consistent. In this case, the reaction was controlled by reaction chemical kinetics. The effectiveness factor related to other chloride density was shown in Figure 7b. Wu and Lai reported that the intrinsic reaction-rate constant of the two-phase allylation reaction using tetra-*n*-butylammonium bromide as a catalyst is calculated to be 1.25(min·kmol/m^3)$^{-1}$ at 40ºC.[14] This finding shows that the reactivity of the triphase catalyst is larger than that of the two-phase catalyst. This result is consistent with the fact that higher lipophilicity of the tertiary amine has higher reactivity for the allylation of phenol.

Wu and Wang reported that the effectiveness factor for single fluid-solid systems was larger than that for the liquid-solid-liquid triphase systems.[9] The ratio of triphase to single fluid-solid effectiveness factor was given as:

$$\lambda = \frac{\eta_{triphase}}{\eta_{fluid-solid}} = \frac{r_{triphase}}{r_{fluid-solid}}. \tag{10}$$

In Eq. 9, the tortuosity τ, reported to vary between 2 and 10,[21] was set at an average value of 6. The porosity ε of the ion-exchange resin was around 0.5.[10] The effective diffusivities calculated by Eq. 9 and by the correlation equation ($[D_e = (\varepsilon/2 - \varepsilon)D]$) for aqueous ion exchange resin[22] were 1.2 × 10^{-8} m^2/min and 4.8 × 10^{-8} m^2/min, respectively. These values were substituted into Eq. 8. Both Thiele modulus calculated were 1.96 × 10^{-2} and 9.8 × 10^{-3} when the chloride concentration was 3.99x × 10^{-4} kmol/m^3. However, both $\eta_{fluid-solid}$ values calculated from Eq. 7 approached to one (>0.99). The $\eta_{triphase}$ value was calculated from Figure 7b. The λ value calculated for different structures for chloride concentration of 3.99 × 10^{-4} kmol/m^3, 1.43 × 10^{-3} kmol/m^3, 3.74 × 10^{-3} kmol/m^3, 1.13 × 10^{-2} kmol/m^3, and 1.12 × 10^{-2} kmol/m^3 were 1.00, 0.468, 0.313, 0.189, and 0.21, respectively. They were less than one and decreased with increasing chloride concentration of the catalyst in the same structures of polymer-supported resin, and were as low as 0.21. It is thus demonstrated that the diffusion resistance in the triphase reaction system was larger than that in the theoretical fluid-solid system.

Reactivity of polymer-supported resin activating with tertiary amine

Although the reactivity of the catalyst was increased with increasing lipophilicity of the tertiary amine, the tri-*n*-octylamine was difficult to immobilize on the polymer-supported resin. Hence, tri-*n*-butylamine and tri-*n*-hexylamine were chosen to study their reactivity in this study. Figure 9 shows the relationships between the formation rate of the product and the

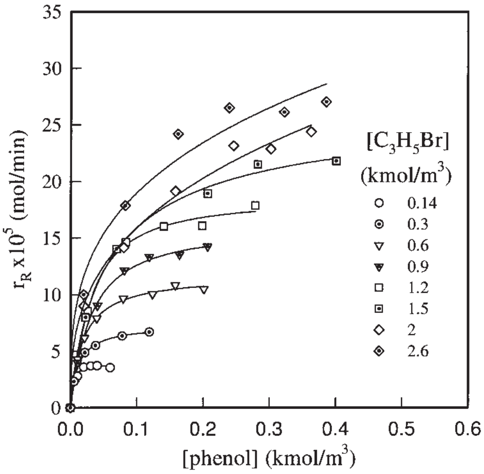


Figure 9. Plot of phenol concentration on the initial reaction rate at different concentrations of C_3H_5Br.

0.5 g catalyst (RS10%, CL2%) immobilized 6 days by 1 kmol/m^3 trihexylamine methanol solution, 40°C, 400 rpm; aqueous phase 50 cm^3: phenol = 0.0085 mol, NaOH = 0.02 mol; organic phase (1,2-$C_2H_4Cl_2$) 50 cm.^{3}

concentration of the phenolate ion at different concentrations of allyl bromide using polymer-supported resins with activating with tri-*n*-butylamine as a triphase catalyst. The r_R value was increased with increasing concentrations of phenolate ion and allyl bromide. At high phenolate concentration, the r_R value remained constant, and all the active sites may be occupied by phenolate ions.

A definition of $r_{R,max}$ is the maximum formation rate for a certain concentration of phenolate ion, and here the $r_{R,max}$-value was increased with increasing concentrations of allyl bromide (Figure 10). The $r_{R,max}$ value increased when the concentration of allyl bromide increased up to 2.0 kmol/m^3. This finding reveals that the formation rate was increased with increasing the amount of allyl bromide. The $r_{R,max}$ value remained around 2.68×10^{-4} mol/min when the concentration of allyl bromide and phenolated ion were more than 0.4 kmol/m^3 and 2.6 kmol/m^3, respectively. The molar active site of the catalyst was 4.78×10^{-4} mol (= w[Cl^-] = 0.5g × 0.956×10^{-3} mol/g). The turnover number, which is defined as the maximum consumed mole of the substrate per catalyst mol per time (= $r_{R,\max}/(M_c \cdot Cl^-)$), was also calculated to be 9.34×10^{-3} s^{-1} at 40°C.

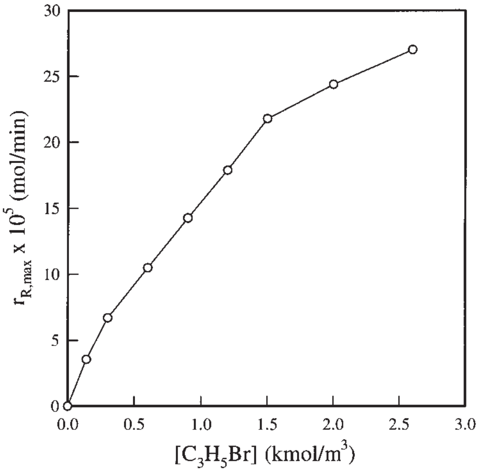


Figure 10. Plot of the maximum initial reaction rate on C_3H_5Br concentration.

The operated conditions are the same as those in Figure 9.

In a similar procedure, the allylation of phenol was conducted using polymer-supported resin with activating with tri-*n*-hexylamine as a triphase catalyst. The $r_{R,max}$ value remained around 2.7×10^{-4} mol/min when the concentration of allyl bromide and phenolated ion were more than 0.4 kmol/m^3 and 3.0 kmol/m^3, respectively. The molar active site of the catalyst was 3.59×10^{-4} mol (= w[Cl^-] = 0.5g × 0.717×10^{-3} mol/g), and the turnover number was also 1.25×10^{-2} s^{-1} at 40°C. The reactivity of the catalyst activating with tri-*n*-hexylamine was larger than that with tri-*n*-butylamine. This finding demonstrates that the order of magnitude for the catalysts activating with tri-*n*-butylamine and tri-*n*-hexylamine corresponds to the result of Wu and Wang using quaternary ammonium polymer-supported resin as the catalyst in the liquid-solid-liquid PTC reaction.[9]

Conclusions

The allylation of phenol was employed as a model reaction to obtain catalytic activities of poly(styrene-*co*-chloromethylstyrene) quaternary ammonium salt as phase-transfer catalyst in a liquid-solid-liquid triphase reaction system. First, the best immobilization condition of polymer-supported resin activating with tertiary amine was obtained: the concentration of tertiary amine was 1 kmol/m^3 in methanol for 24 h, and the trihexylamine was the best reactivity among tertiary amines. The proper amount of catalyst in this geometric reaction system was 0.3∼1 g. Furthermore, putting the active site on the surface zone of the catalyst may reduce the diffusion effect of the reactant within the catalyst. However, the surface structure of the catalyst was highly hydrophilic to increase the imbibed water content so as to decrease the reactivity of allylation of phenol. On the other hand, it is an effective method since the reduced active site of the catalyst for the same degree of ring substitution (that is, RS 20%, 4%) obviously increased the reactivity of allylation of phenol. Finally, the immobilized chloride density (active site) in the resin was decreased with increasing carbon number of tertiary amines. However, the reactivity of the catalyst was increased with increasing carbon number of tertiary amine. According to the turnover number, the polymer-supported resin activating with trihexylamine was a better catalyst than that with tributylamine. The polymer-supported resin activating with trihexylamine may be the focus of future study on the triphase reaction.

Acknowledgments

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Notation

a = total wetted surface area of the catalyst, m^2
a′ = surface area per dry catalyst, m^2/g
C_{As} = concentration at the surface of the pellet, kmol/m^3

[Cl$^-$] = chloride density of the catalyst, mmol/g
CL = degree of crosslinkage, %
CMS = chloromethylstyrene
D = bulk diffusivity of reactant, $m^2.min^{-1}$
De = effective diffusivity of reactant, $m^2.min^{-1}$
DMF = N,N-dimethylformamide
k = reaction rate constant, $(kmol/m^3{\cdot}min)^{-1}$
m_p = weight of polymer, g
m_{si} = weight of solvent, g
PhOR = allylphenyl ether
r = reaction rate, $kmol/(m^3{\cdot}min)$
r_R = initial reaction rate, $kmol/(m^3{\cdot}min)$
$R_{avg,wet}$ = average radius of wetted pellet of catalyst, m
RS = degree of ring substitution, %
t = reaction time, min
V = volume of the solvent, m^3
V_R = volume ratio of wetted catalyst to dry catalyst
w = weight of the catalyst, g
Y = yield of allylphenyl ether

Greek letters

ε = porosity in the resin
ϕ = Thiele modulus for the substitution reaction
η = effectiveness factor
λ = ratio of real to theoretical effectiveness factor
τ = tortuosity in the resin

Subscripts

Avg = average
AS = surface reactant on the surface
e = effective
max = maximum
PhOR = allyl phenyl ether

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