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Mechanism and NaOH effect of polymer-supported catalyst: phosphazene reaction

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Abstract

The mechanism and NaOH effect of the substitution reaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with phenol to synthesize the poly(phenoxy)chlorocyclotriphosphazene were investigated by using triphase catalysis in an organic phase/alkaline solution. Four relationships between the ion-exchange reaction and organic reaction were presented and clarified by experimental result. The reaction behaviors varied with different particle sizes of resins. The reaction zone was not the whole resin, and occurred obviously at a shell of the resin when the resin was used larger particle size and higher degree of crosslinkage. The thickness of shell in the resin varied with different NaOH concentrations. The intrinsic reaction kinetics, particle diffusion and film diffusion had to be considered to explain this triphase reaction behavior. The performance of recycle fixed-bed reactor was also investigated.

Keywords: Phosphazene; Sequential reaction; Phase-transfer catalysis; Triphase catalysis; Reactor design

1. Introduction

The reactivity of a liquid–solid–liquid triphase reaction (i.e. polymer-supported catalytic reaction) is influenced by the structure of the active sites, particle size, degree of crosslinkage, degree of the ring substitution, swollen volume, and spacer chain of a catalyst. In the past, the characteristics of a triphase reaction subjected to the mass-transfer limitation of the reactants and ion-exchange rate in the aqueous phase have been discussed [1–5]. The ion-exchange rate in the aqueous phase affects the reactivity of the triphase reaction.

The hypothesis of planar phase boundary used in a classical two-phase system cannot be derived to describe a triphase system. Telford et al. [3] suggested an alternating shell model that requires periodical changes in the liquid phase filling the pores of the catalyst. Schlunt and Chau [6] indicated that the reaction was occurred in a thin shell near the particle surface. Tomoi and Ford [7] and Hradil et al. [8] presented that the droplet of organic (or aqueous phase) was collided with the solid catalyst. However, the mechanism and effect of the internal molecular structure of the polymer support in a triphase reaction have seldom been discussed. Although some rules were listed in the text and clarified by the experimental result [9,10], the relationship of reaction mechanism between the reaction and polymer resin in a liquid–solid–liquid triphase reaction has not been understood completely. Hence, this study aims to discuss the mechanism of a polymer-supported triphase reaction.

Among the vast scope of phase-transfer catalysis (PTC) application [9,10], approximately 40% of PTC patents involve the hydroxide ion and, it has been estimated that, approximately 60% of commercial PTC application involve the hydroxide ion [10]. Many papers [11–16] have presented that the reactivity of a reactant in an organic reaction is influenced by the base concentration. It is well known that the base concentration plays a crucial role in a liquid–liquid phase-transfer-catalyzed reaction. However, the base effect for the reactivity of reactant in a liquid–solid–liquid triphase reaction was rarely attention.

Most PTC reactions are carried out on an industrial scale in the batch mode in mixer-settler arrangements. In view of the reactor design in the liquid–solid–liquid triphase reaction, Ragaini et al. [17–19] reported the use of the fixed-bed reactors with a recycling pump or with a recycling pump and an ultrasonic mixer, and emphasized the importance of effluent recycle concept. Schlunt and Chau [6] reported the use of a cyclic slurry reactor, which allowed the immiscible reactants to contact the catalyst sites in controlling sequential steps. However, for liquid–solid–liquid triphase system, which reactor type employed properly in this reaction system is not clear solution. In this study, a recycle fixed-bed

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Nomenclature

CL	degree of crosslinkage
k_{app}	apparent reaction-rate constant (cm^3/(min g-resin))
M_{resin}	weight of resin (g)
MX	metallic salt of X
MY	metallic salt of Y
QX	quaternary salt of X ion in the resin
QY	quaternary salt of Y ion in the resin
r	radius of resin
RS	degree of ring substitution
RX	chemical reactant
RY	chemical product
t	reaction time (min)
T	absolute temperature (K)
V_T	total volume of the reaction system (cm^3)
Superscript	
-	species in the organic phase

reaction was used to evaluate the performance of the triphase reaction.

The substitution reaction of $(NPCl_2)_3$ with phenol is a sequential reaction in this study. The reaction type is different from the common one-stage reaction. The experimental results can easily demonstrate the relationship between the reaction kinetic limitation and the particle diffusion limitation. Hence, the purpose of the present study is to investigate the NaOH effect and mass-transfer behavior for synthesizing poly(phenoxy)chlorocyclotriphosphazene from the reaction of phenol with hexachlorocyclotriphosphazene by triphase catalysis in an organic solvent/alkaline solution.

2. Experimental

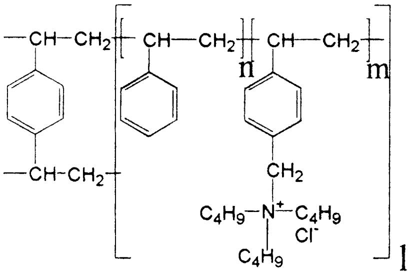
2.1. Materials

Hexachlorocyclotriphosphazene (Aldrich, 99.5%), phenol (Aldrich, 99%), styrene (RDH, 99%), chloromethylstyrene (Aldrich, 97%), divinylbenzene (Aldrich, 80%), tri-*n*-butylamine (Merck, 98%) and other reagents are all analytical chemicals.

2.2. Procedures

2.2.1. Preparation of poly(styrene-co-chloromethylstyrene) immobilized tri-n-butylamine

The synthetic procedure for polymer-supported (styrene–chloromethylstyrene–divinylbenzene) immobilized tri-*n*-butylamine resin is identical to that of Wu and Meng's report [15]. The molecular structure of polymer-supported (styrene–chloromethylstyrene–divinylbenzene) resin is given below:



The properties of microporous resin with 4 mol% of crosslinkage and 20 mol% of ring substitution are: apparent density = 1220 kg/m^3, true density = 702 kg/m^3, Cl^- density = 0.7 mmol/g (determined by Volhard method). The characteristics of the resin were similar to the Wu and Lee's report [20].

The procedure for determining imbibed solvent composition of the resin is similar to that in Wang and Wu's report [21]. A 125 cm^3 funnel equipped with a fitted disk served as the testing apparatus. A known quantity of the catalyst pellet, organic solvent and alkaline solution were added to the funnel. Then, the external liquid phase was removed from the slurry using an aspirator. The wet resin was placed in a flask containing 15 cm^3 of dimethylformamide from the catalyst pellets. The amounts of solvent and water in dimethylformamide were measured by HPLC and potential meter (Karl Fischer Titration), respectively.

2.3. Synthesis of poly(phenoxy)chlorocyclotriphosphazene: $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1$–6

The procedure for the synthesis of poly(phenoxy)chlorocyclotriphosphazene is previously described [22]. The products of $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1$–6, were successfully separated by pressurized column chromatography and cooling crystallization. On the basis of ^{31}P and H NMR spectra, the substitution reaction type belongs to a trans-nongeminal path.

2.4. Kinetics of the triphase catalytic reaction

The analytical method and the kinetic procedure of poly (phenoxy)chlorocyclotriphosphazene were previously described [22]. The standard reaction conditions in batch reactor were: NaOH = 0.9 kmol/m^3, C_6H_5OH = 0.75 kmol/m^3, H_2O = 50 vol.% (75 cm^3), $(NPCl_2)_3$ = 0.575 kmol/m^3, CH_2Cl_2 = 50 vol.%, 20 °C, resin (microporous, 4 mol% CL, 20 mol% RS, 60–80 mesh) = 0.5 kg/m^3, Cl^- = 0.7 mmol/g, 1000 rpm. The apparatus of recycle fixed-bed reactor was a Pyrex jacketed flask, shown in Fig. 1. The standard reaction conditions were NaOH = 0.9 kmol/m^3, C_6H_5OH = 0.75 kmol/m^3, H_2O = 50 vol.% (75 cm^3), $(NPCl_2)_3$ = 0.575 kmol/m^3, CH_2Cl_2 = 50 vol.%, 20 °C, resin (microporous, 4 mol% CL, 20 mol% RS, 60–80 mesh)

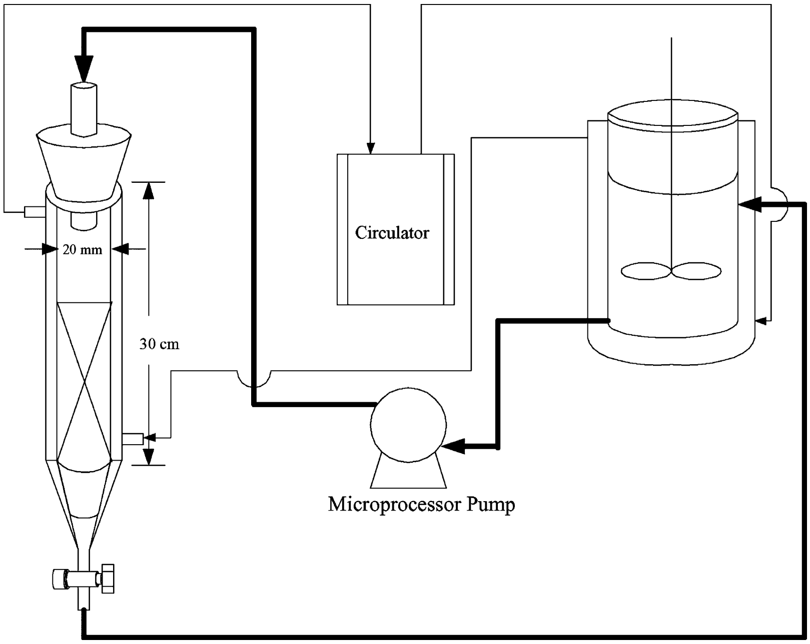
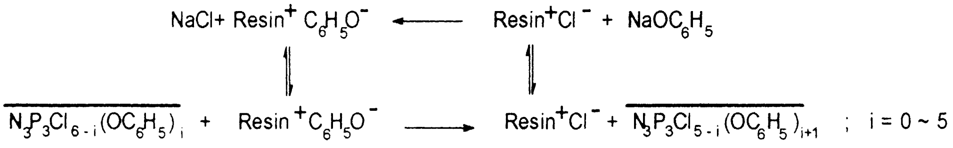


Fig. 1. Fixed-bed with recirculating pump reactor.

$= 13.3\,\mathrm{kg/m^3}$, $\mathrm{Cl^-} = 0.7\,\mathrm{mmol/g}$, 1000 rpm, flow rate $= 7.5\,\mathrm{cm^3/min}$.

3. Results and discussion

In a triphase reaction, the overall kinetic cycle can be broken up into two steps by virtue of the presence of two practically insoluble liquid phases: a chemical conversion step in which the active catalyst sites (resin$^+$ with phenolate ions) react with the hexachlorocyclotriphosphazene in the organic solvent, and an ion-exchange step in which the attached catalyst sites are in contact with the aqueous phase:



$$\begin{tikzcd} \mathrm{NaCl + Resin^+C_6H_5O^-} \arrow[d, shift left] & \mathrm{Resin^+Cl^- + NaOC_6H_5} \arrow[l] \arrow[d, shift left] \\ \overline{\mathrm{N_3P_3Cl_{6-i}(OC_6H_5)_i}} + \mathrm{Resin^+C_6H_5O^-} \arrow[u, shift left] \arrow[r] & \mathrm{Resin^+Cl^-} + \overline{\mathrm{N_3P_3Cl_{5-i}(OC_6H_5)_{i+1}}} \arrow[u, shift left] \end{tikzcd} \quad ; \quad i = 0 \sim 5 \qquad (1)$$

The overbar denotes the characteristics of the species in the organic phase. Thus, the total moles of catalyst sites are:

$$\mathrm{resin_T} = \mathrm{resin^+C_6H_5O^-} + \mathrm{resin^+Cl^-} \qquad (2)$$

In this study, the reaction rates for the organic phase and the aqueous phase follow pseudo-first-order kinetics [15,22] and can be written as follows:

$$-\frac{\mathrm{d}\overline{[(\mathrm{NPCl_2})_3]}}{\mathrm{d}t} = \bar{k}_{\mathrm{app}} \frac{M_{\mathrm{resin}}}{V_{\mathrm{T}}} \overline{[(\mathrm{NPCl_2})_3]} \qquad (3)$$

and

$$-\frac{\mathrm{d}[\mathrm{NaOC_6H_5}]}{\mathrm{d}t} = k_{\mathrm{app}} \frac{M_{\mathrm{resin}}}{V_{\mathrm{T}}} [\mathrm{NaOC_6H_5}] \qquad (4)$$

where $\bar{k}_{\mathrm{app}}$ and k_{app} ($\mathrm{cm^3/(min\,g\text{-}resin)}$) represent the apparent reaction-rate constant in the organic phase and aqueous phase, respectively. The values of pseudo-first-order kinetics are applied up to 90–100% conversion of $(\mathrm{NPCl_2})_3$, depending on reaction conditions. The consumption rate of $\mathrm{NaOC_6H_5}$ in the aqueous phase is equal to the total consumption rate of the intermediate products and reactant. Hence, Eq. (3) is independent of Eq. (4). Because the apparent reaction rate varied proportionately with the amount of polymer-supported quaternary ammonium chloride, the first-order dependence on the amount of triphase catalyst.

The function of base in a liquid–solid–liquid triphasic reaction have four roles: (i) reactant; (ii) deprotonation of acidic organic compound to become the reactive form; (iii) improving the reactive environment in the catalytic pellets, such as swelling volume, imbibed solvent ratio, solubility between two phases, etc.; or (iv) reducing the solvation of catalyst and water to upgrade the reactivity of active catalyst in the organic phase. In previous works, it was observed that the reactivity of organic reactant varied with the concentration of the base in a liquid–liquid phase-transfer-catalyzed reaction [13,23,24]. In the liquid–solid–liquid triphase reaction, the effect of base for the reactivity of reactant (or reactive environment) was rarely attention. Fig. 2 shows

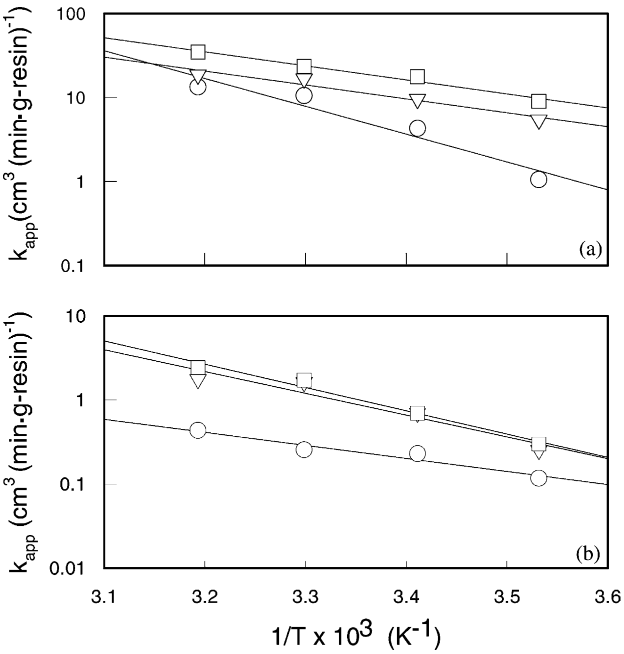


Fig. 2. Arrhenius plot of apparent reaction-rate constants $\bar{k}_{app}$ and k_{app} on temperature; NaOH: (○) 0.5 kmol/m^3, (▽) 0.9 kmol/m^3, (□) 1.8 kmol/m^3.

the influence of NaOH salt on the apparent reaction-rate constants $\bar{k}_{app}$ and k_{app}. The values of $\bar{k}_{app}$ and k_{app} dramatically increase with increasing concentration of NaOH when the ratio of NaOH to C_6H_5OH is in the range of 1–1.5. This trend corresponds to that using liquid–liquid phase-transfer catalysis [15]. Table 1 lists that the apparent activity energies of Arrhenius law for the organic phase and the aqueous phase at different NaOH concentration. The apparent activity energies for organic reaction decreased, and for aqueous reaction increased when the NaOH concentration increased. The reactive behavior of organic reaction became reaction chemical control to diffusion control ($E_a < 42$ kJ/mol). The reports of Wang and Wu [25] and Wu and Lee [20] indicated that the imbibed solvent compositions of organic solvent, water and salt, and the swollen volume of resin increased with increasing the NaOH concentration. In other words, the reactive environment of organic reactant near the active site increased with increasing NaOH concentration. However, the activity energy of the ion-exchange reaction increased when the NaOH concentration increased. The reactive behavior of ion-exchange reaction became diffusion control to the reaction chemical control. The NaOH concentration was excess to derive the hydroxide ion to react with resin$^+$Cl$^-$ to form resin$^+$OH$^-$, and so that was larger than that of phenolate ion in the resin. Thus, the ion-exchange rate of $C_6H_5O^-$ with resin$^+$Cl$^-$ decreased.

Table 1
Apparent activation energies in the organic and aqueous reaction on different NaOH concentrations and particle sizes

	[NaOH] (kmol/m^3)			Mesh	
	0.5	0.9	1.8	60–80	140–200
$\bar{E}_a$ (kJ/mol)	62.4	31.3	31.5	31.5	18.0
E_a (kJ/mol)	29.3	48.9	52.3	52.3	9.60

The concept of phase-plane and superposition [22] was used to change the variable from time to the consumed ratio of $C_6H_5OH/(NPCl_2)_3$ in Fig. 3. Fig. 3 displays the trajectories of the products and the reactant in terms of mole ratio of $C_6H_5OH/(NPCl_2)_3$ consumed. In the organic phase, the reaction mechanism of the reaction of $(NPCl_2)_3$ with resin$^+C_6H_5O^-$ can be expressed by Eq. (1). The expression cannot be directly solved to yield compositions as a function of time because the amount of resin$^+C_6H_5O^-$ in the resin was unknown, and the reaction was also influenced by mass-transfer resistance. If the mass-transfer resistance of the poly(phenoxy)chlorocyclotriphosphazene in the interior of the resin can be neglected, the maximum yield of monophenolated product can be obtained when, approximately 1 mol of phenol per mol of $(NPCl_2)_3$ has been reacted, and the maximum yield of diphenolated product results when around 2 mol of phenol per mol of $(NPCl_2)_3$ has been reacted, etc. Whereas, if the position of the maximum yield shifts to right, the higher shifting value means a larger mass-transfer resistance of organic reactant in the particle. In Fig. 3, the maximum yield of monophenolated product shifts to right by more 0.2 units; the maximum yield of diphenolated product shifts to right by more 0.1 units. This reveals that the intraparticle diffusion on the organic reaction rate influence the reaction rate. The trend of shifting to the right of the maximum yield increased with increasing concentration of NaOH.

The reactivity of a triphase reaction is influenced by the structure of the active sites, particle size, degree of crosslinkage, degree of the ring substitution, swollen volume, and spacer chain of a catalyst pellet. All these make the triphase reaction a complicate one. Past efforts have carried out this investigation macroscopically. However, the mechanism and effects of the internal molecular structure of the polymer support have seldom been discussed.

According to the steric effect of phenolate ion reacting with hexachlorocyclotriphosphazene and the Wu and Meng's reports (two-phase catalysis [22]; triphase catalysis [15]), the maximum yield of partially substituted phenolated product increased with increasing degree of substitution reaction. Fig. 3 shows that the maximum yield of monophenolated product was larger than that of diphenolated product, and the maximum yield of partially phenolated product decreased when the NaOH concentration increased (i.e. reactivity of the active site increased). This result reveals that the reaction rate of phenolate reacting with monophenolated (or diphenolated) product was larger than the diffusion rate of monophenolated (or diphenolated) product from active site to bulk solution and hexachlorocyclotriphosphazene from bulk solution to active site. Most monophenolated (or diphenolated) product reacted in situ with resin$^+C_6H_5O^-$ in the neighborhood of the active site.

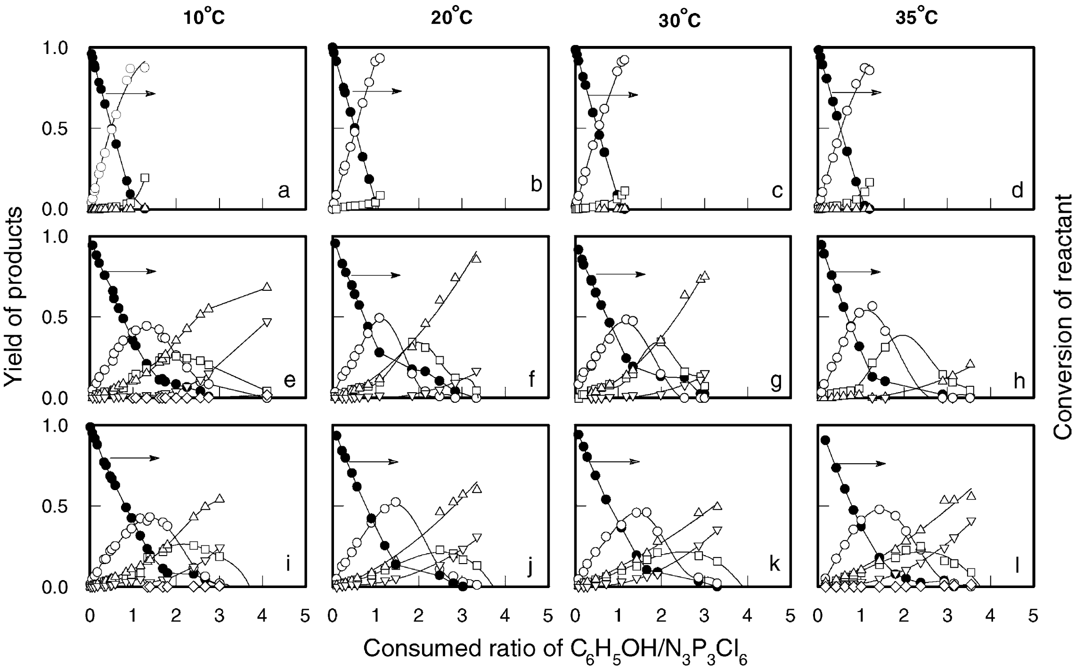


Fig. 3. Yields of products and conversion of reactant as a function of reactant $C_6H_5OH/(NPCl_2)_3$ consumption ratio at different NaOH concentration: (a–d) 0.5 kmol/m^3, (e–h) 0.9 kmol/m^3, (i–l) 1.8 kmol/m^3; (●) $(NPCl_2)_3$, (○) $N_3P_3Cl_5(OC_6H_5)_1$, (▽) $N_3P_3Cl_4(OC_6H_5)_2$, (□) $N_3P_3Cl_3(OC_6H_5)_3$, (◇) $N_3P_3Cl_2(OC_6H_5)_4$, (△) $N_3P_3Cl(OC_6H_5)_5$.

Meantime, when the reactivity of resin$^+C_6H_5O^-$ increased as the NaOH concentration increased, the diffusion resistance of reactants was obvious.

In general, the reaction mechanism of the fluid–solid reaction is: (i) mass transfer of reactants from the bulk solution to the surface of the catalyst pellet; (ii) diffusion of reactant to the interior of the catalyst pellet (active site) through pores; (iii) intrinsic reaction of reactant with active sites. Triphase catalysis is more complicated than traditional heterogeneous catalysis, because it involves not merely 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. For step (iii), the substitution reaction in the organic phase and ion-exchange reaction in the aqueous phase occurred.

In the present reaction, the overall reaction includes the organic substitution and the aqueous ion-exchange reaction (Eq. (1)). Two rate-controlling steps influence the reaction rate simultaneously. The reaction is complicated. Hence, in views of literatures [1,3,7,15,16,26,28], the four special relationships between the ion-exchange reaction and organic reaction with an increasing concentration of organic reactant $(NPCl_2)_3$ according to Eqs. (1)–(4) are discussed as follows:

(i) It is assumed that the ion-exchange rate in the aqueous phase is much higher than the substitution reaction rate in the organic phase. The effect of ion-exchange reaction could be eliminated from the reaction-controlling steps. Also,

(a) the intrinsic organic reaction is the rate-controlling step. Hence, the concentration of the active site of triphase catalyst resin$^+C_6H_5O^-$ remains constant. The value of $\bar{k}_{app}$ is constant. The value of k_{app} increased with higher concentration of $(NPCl_2)_3$ due to an increase in the consumption rate of phenolate ion (Fig. 4a). Similar result was presented by Wu and Tang [16];

(b) the organic reaction rate is limited by both reaction kinetics and particle diffusion. The values of k_{app} increase, and the values of $\bar{k}_{app}$ decrease with an increasing concentration of $(NPCl_2)_3$ (Fig. 4b) [26];

(c) the organic reaction rate is only limited by film diffusion of reactant from the bulk organic solution to the surface of the catalyst pellet is the rate-controlling step. The values of $\bar{k}_{app}$ is constant, and the values of k_{app} dramatically increase with an increasing concentration of $(NPCl_2)_3$ (Fig. 4c). Similar result was presented by Tomoi and Ford [7].

(ii) It is assumed that the organic reaction rate in the organic phase is much higher than the substitution reaction rate in the organic phase. The effect of the organic reaction could be eliminated by controlling the reaction. Also,

(a) if the film diffusion of ion from the bulk aqueous solution to the surface of the catalyst pellet is the rate-controlling step, the value of k_{app} remains constant because the initial concentration of

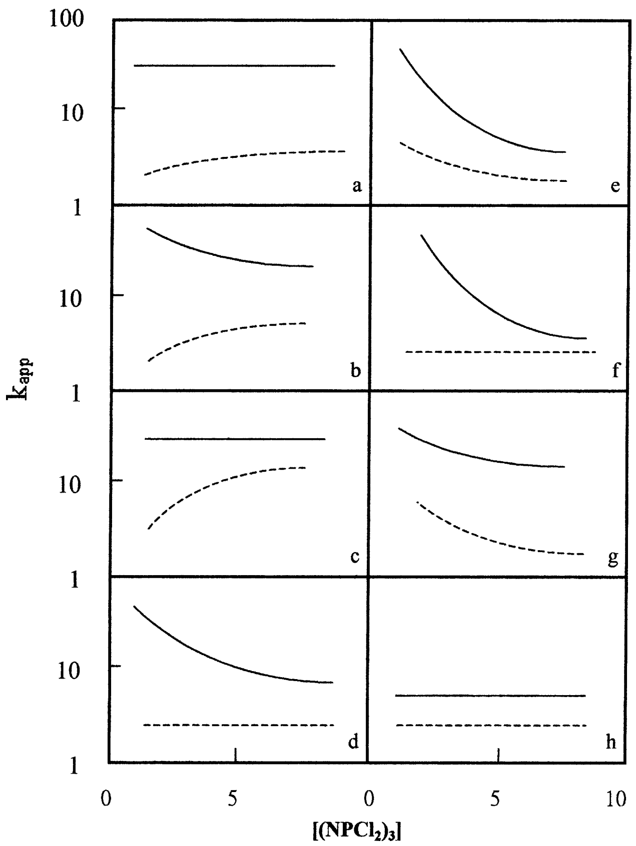


Fig. 4. Order of magnitudes of relationships of $\bar{k}_{app}$ (solid line) and k_{app} (dashed line) on $(NPCl_2)_3$ concentrations.

phenolate ion is kept constant, and the value of $\bar{k}_{app}$ dramatically decreases (Fig. 4d) [26];

(b) if the ion-exchange rate is limited by both particle diffusion and film diffusion, the value of k_{app} decreases with increasing $(NPCl_2)_3$ concentration, and the value of $\bar{k}_{app}$ dramatically decreases (Fig. 4e). When the degree of ring substitution is low, the ion-exchange process is the rate-limiting step [1,3,27,28];

(c) if the ion-exchange rate is limited by the intrinsic ion-exchange rate, the value of k_{app} remains constant with an increasing $(NPCl_2)_3$ concentration, and the value of $\bar{k}_{app}$ dramatically decreases (Fig. 4f).

(iii) If the organic reaction rate is limited by both reaction kinetics and particle diffusion, and the ion-exchange rate is also limited by film (or particle) diffusion, the value of k_{app} decreases, and the value of $\bar{k}_{app}$ also decreases (Fig. 4g) [15].

(iv) When the organic reaction rate competes with the ion-exchange rate, the values of k_{app} and $\bar{k}_{app}$ remain almost constant with increasing concentration of $(NPCl_2)_3$ (Fig. 4h).

If mass-transfer resistance influences the reaction, the concentration of the active catalyst cannot remain constant during the course of the reaction. Also, when the concentration of organic reactant decreases, both the reaction rate and the effect of mass transfer of organic or aqueous reactant between solid and liquid phase decrease. However, the apparent first-order reaction-rate constant increased with decreasing the concentration of organic reactant [15,26]. The experimental data in Fig. 5 shows two different phenomenon observed, and their apparent first-order reaction-rate constants were

(a) decreased with increased concentration of organic reactant when the particle size of the resin was smaller than 104 μm. The ratios of k_{app} (or $\bar{k}_{app}$) for $(NPCl_2)_3$ = 0.28–4.3 mmol are less than 2 in Fig. 5d and h. Hence, this reaction belongs to case (iii). The ion-exchange rate could not be neglected despite the concentration ratio of $NaOC_6H_5$ to $(NPCl_2)_3$ being greater than 12. The ion-exchange step in the aqueous phase should be taken into account when studying the triphase reaction rate.

(b) otherwise, kept constant (or increased slightly) when the particle size of the resin was larger than 104 μm (Fig. 5a–c and e–g), and the reaction belongs to case (iv).

The elemental analysis of the resin was studied by means of energy dispersive X-ray spectrometer (EDS) methods. The elemental analysis of EDS of the catalyst (microporous, 4 mol% of crosslinkage, 20 mol% of ring substitution) observed before reaction shows that a high Cl peak was detected due to the active site. Some chemical compounds (Si, Ca) added in the procedure of synthesizing the polymer resin were also detected. Although the pretreatment of the resin was conducted by washing with water, NaOH solution and acetone, the salts (Si, Ca) used as reaction agent by the suspension method were slightly retained in the resin. After reaction of 4 h, the elemental analysis of EDS of the catalyst shows that a low Cl peak was detected due to the active site. The peak height for Cl atom was decreased 72% and for O atom increased 54% between before and after the reaction. The finding demonstrates that the phenoxide ion exchanged the chloride ion as counter ion on the polymer-supported catalyst during the course of the reaction, and however, did not occupy all the active site in the catalyst. Hence, the result reveals that the mass-transfer resistance of the ion-exchange step influenced the concentration of phenoxide ion on the active site ($resin^+C_6H_5O^-$).

The surface area of dry catalyst measured by BET absorption method was smaller than 0.01 m^2/g for 4 mol% crosslinkage and 20 mol% of ring substitution resin. However, the volume and wet porosity of catalyst were increased about three times when the different catalysts interact differently with the volume ratios of organic phase to aqueous phase. Wu and Lee [20] indicated that the imbibed amount of organic solvent was larger than that of water because the structure of the catalyst support is lipophilic. The imbibed amount of water was dependent on the amount of ammonium cation (i.e. active site). Hence, the imbibed amount of

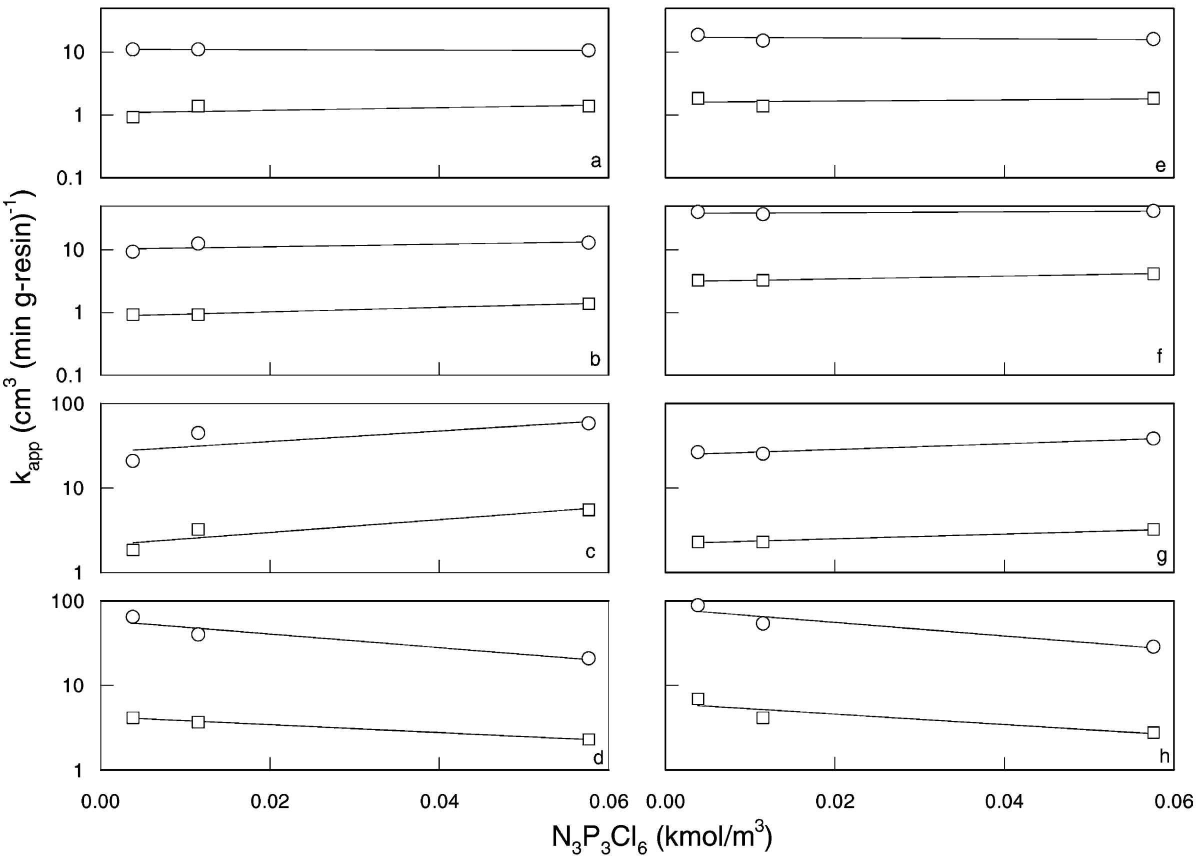


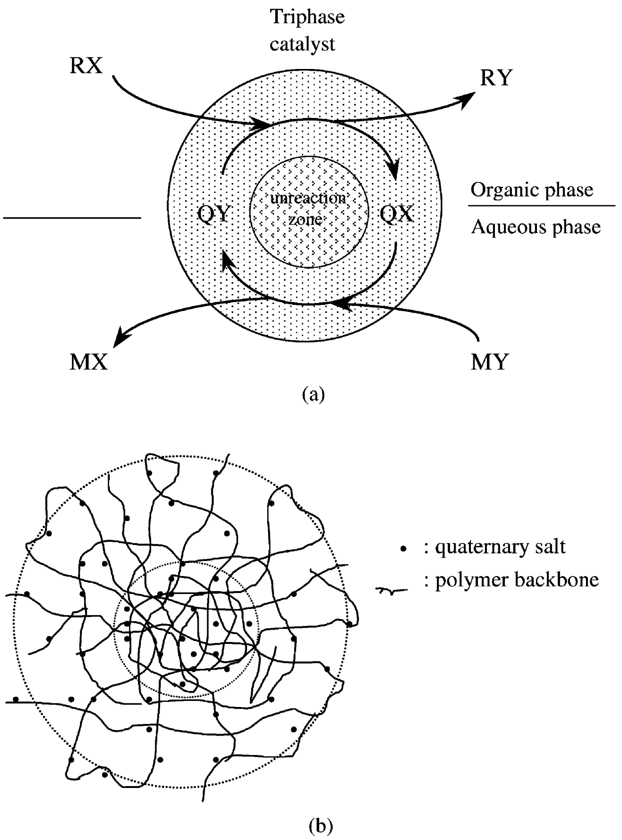
Fig. 5. Relationships of $\bar{k}_{app}$ (○) and k_{app} (□) on $(NPCl_2)_3$ concentrations at different NaOH concentrations: (a–d) 0.9 kmol/m^3, (e–h) 1.8 kmol/m^3; the particle sizes of the resins: (a, e) 45–60 mesh, (b, f) 60–80 mesh, (c, g) 80–150 mesh, (d, h) 150–200 mesh.

water increased with increasing number of ring substitution. If the structure of resin is rigid (higher degree of crosslinkage) or larger particle size, the organic phase and the aqueous phase were almost quiet in the interior of the resin. The organic and aqueous reactants should not diffuse simultaneously to the active site. Hence, the reaction occurs at a shell near the surface of the resin. When the degree of crosslinkage of the resin is low, the structure of the resin was not solid. The flow rates of the organic solution and the aqueous solution in the interior of the resin increase with increasing agitation rate. The number of the effective active site in the resin is increased.

Wu and Lee [20] indicated that the free chloride ions on the active site (measured by Volhard analysis) were at only 50–70% of the amount of immobilized content (measured by element analysis). The results of the Volhard analysis method determined the free chloride ions in the bulk solution by the $AgNO_3$ titration method. Their result implied that the active site in the resin could not react completely with organic reactant in the duration of triphase reaction. According to the experimental result, this reaction is a two-zone model (or shell-core model). The reaction occurs in a shell-zone, and does not occur in a core-zone. Therefore, the triphasic reaction mechanism and the swollen type of the resin can be given in Fig. 6.

Fig. 5c and g show that the k_{app} (or $\bar{k}_{app}$) increases with increasing concentration of $(NPCl_2)_3$. According to Fig. 5c and g, and Eqs. (3) and (4), the concentrations of both $resin^+Cl^-$ and $resin^+C_6H_5O^-$ increase with increasing $(NPCl_2)_3$ concentration. This finding may demonstrate that the reaction zone was not the whole resin during the course of reaction, and was slightly increased and shifted to central of the resin when the $(NPCl_2)_3$ concentration increased. Furthermore, if the organic reactant concentration is extrapolated to zero ($[\overline{(NPCl_2)_3}] \to 0$), the organic reaction rate is much smaller than the mass-transfer rate of organic or aqueous reactant between catalyst particle and liquid phase. Hence, the effect of mass transfer can be neglected. The reaction-rate constant deduced at $[\overline{(NPCl_2)_3}] \to 0$ increased when the particle size decreased (Fig. 5), that is the effective active site in the resin participating into the triphasic reaction increased. The reaction-rate constant determined from the intercept in Fig. 5d were around 78.5 cm^3/(min g-resin), which supposed all active site to react with organic reactant. Wu and Meng [22] reported the intrinsic reaction-rate constant using tetra-*n*-butylammonium bromide as phase-transfer catalysis was 3712 m^3/(kmol min). Hence, the amount of the active site $resin^+C_6H_5O^-$ participating in the triphasic reaction may equal 0.02 mmol/(g-resin) (=78.5/3712). The effective percentage of the active site in the resin is only 3% (= 0.02/0.7 × 100) because the Cl density in the resin was 0.7 mmol/(g-resin). In general, the reactivity of tetra-*n*-butylammonium bromide is larger than that of polymer-supported ammonium bromide. Hence, the effective percentage of the active site in the resin is larger than 3%, but smaller than 100%. These results indicate that the active size of the resin was not all participated to react with the reactant at different particle size during the course of reaction. The reaction zone was at a shell of the resin. Therefore, according to the experimental result, we deduce again the reaction mechanism in the triphase reaction.

The rate-controlling step can be identified experimentally without much difficulty. Internal reaction control is established when the overall rate is proportional to the amount of catalyst and is independent of the particle size. With both film diffusion and surface reaction control the rate is inversely proportional to the particle size. Fig. 7 shows the effects of particle size of catalyst resin on the apparent reaction-rate constant. The reaction-rate constant was almost proportional to the reciprocal of radius of the resin (i.e. the ratio of area to volume) when the particle size was larger than 104 μm (Fig. 7). Hence, the reaction may be influenced by both film diffusion and surface reaction. Another, Table 1 shows that the apparent activity energies of the reactions for larger particle (60–80 mesh) are larger than those for smaller particle (150–200 mesh). Because the reaction zone of shell and the ratio of area to volume of the catalyst pellet increased



(a)

(b)

Fig. 6. Mechanism of the triphasic reaction (a) and the swollen type of the resin (b).

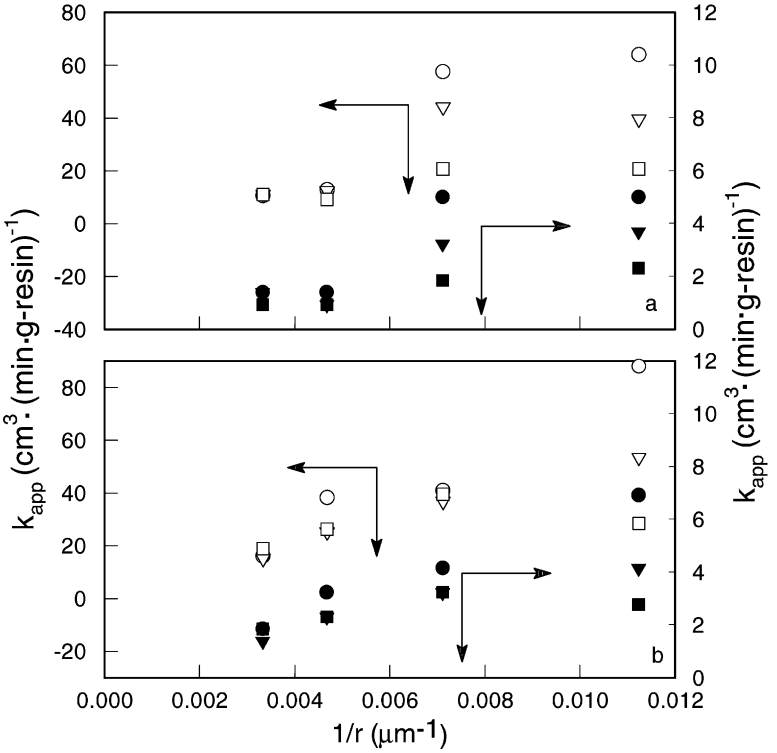


Fig. 7. Effect of particle size on $\bar{k}_{app}$ and k_{app} for different NaOH concentrations: (a) 0.9 kmol/m^3, (b) 1.8 kmol/m^3; the $(NPCl_2)_3$ concentrations: (○) 5.76 × 10^{-2} kmol/m^3, (▽) 1.15 × 10^{-2} kmol/m^3, (□) 3.84 × 10^{-3} kmol/m^3.

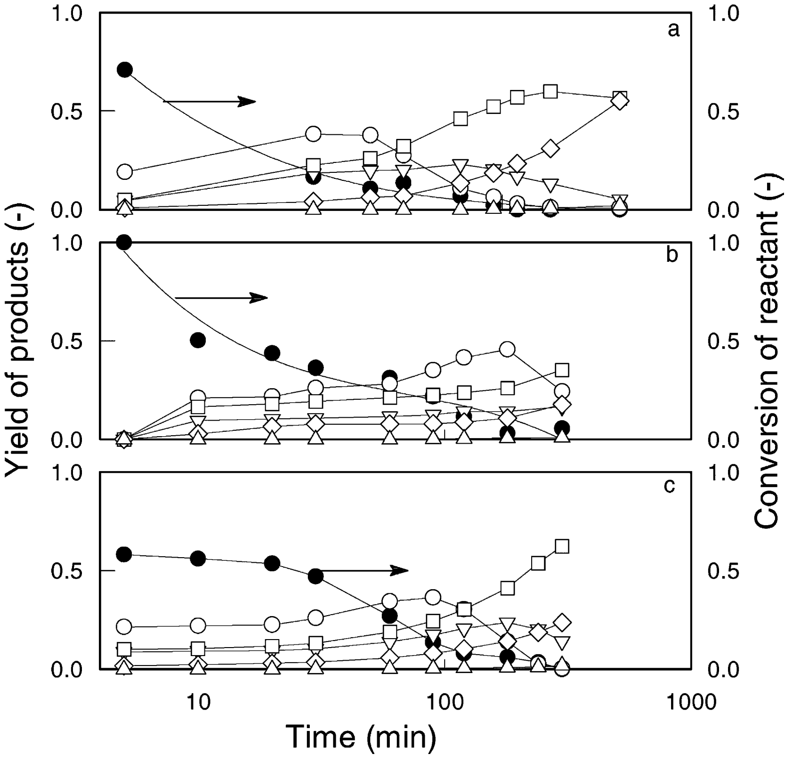


Fig. 8. Performance of batch reactor: (a) resin = 0.6 g; recycle fixed-bed reactor: resin (CL: 4 mol%, RS: 20 mol%) = 2.0 g; flow rate: (b) 1.5 cm^3/min, (c) 7.5 cm^3/min; (●) $(NPCl_2)_3$, (○) $N_3P_3Cl_5(OC_6H_5)_1$, (▽) $N_3P_3Cl_4(OC_6H_5)_2$, (□) $N_3P_3Cl_3(OC_6H_5)_3$, (◇) $N_3P_3Cl_2(OC_6H_5)_4$, (△) $N_3P_3Cl(OC_6H_5)_5$.

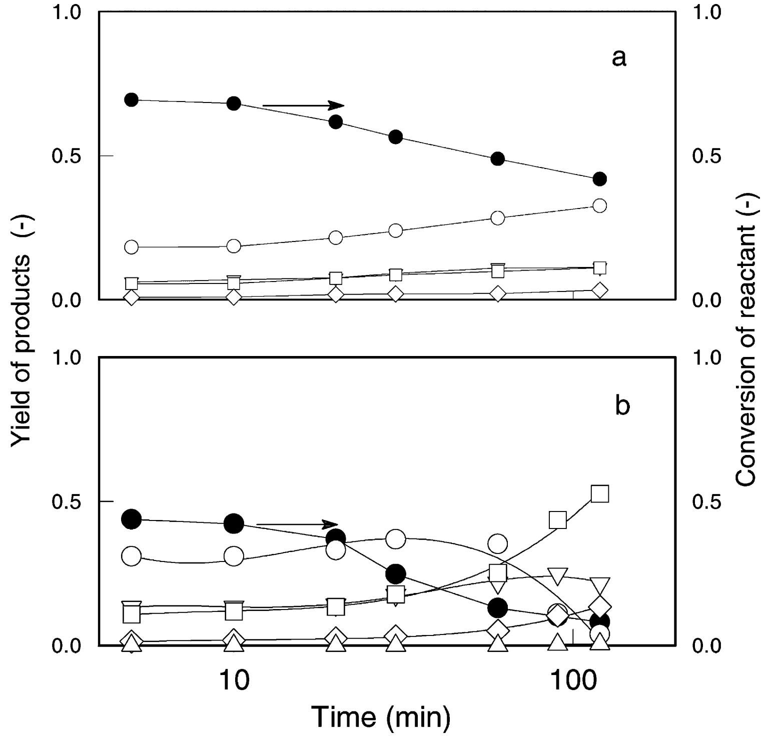


Fig. 9. Effect of recycle ratio: (a) 0 and (b) ∞ in recycle fixed-bed reactor: resin (CL: 4 mol%, RS: 40 mol%) = 2.0 g; flow rate = 7.5 cm^3/min; (●) $(NPCl_2)_3$, (○) $N_3P_3Cl_5(OC_6H_5)_1$, (▽) $N_3P_3Cl_4(OC_6H_5)_2$, (□) $N_3P_3Cl_3(OC_6H_5)_3$, (◇) $N_3P_3Cl_2(OC_6H_5)_4$, (△) $N_3P_3Cl(OC_6H_5)_5$.

with decreasing particle size of the resin, the diffusion resistance for smaller particle was more serious. The resins used were microporous, 2 mol% of crosslinkage and 20 mol% of ring substitution in previous works [15], and microporous, 4 mol% of crosslinkage and 20 mol% of the number of ring substitution in this study. Comparing both experimental results, the high degree of crosslinkage increased the particle diffusion resistance of reactants in this reaction system.

The technique of fixed-bed reactors for triphase reaction had an insufficient mixing of the two liquid phases when they flow through the catalytic bed. The apparatus of recycle fixed-bed reactor was a Pyrex jacketed flask in this study as shown in Fig. 1. Fig. 8 shows the performance of batch reactor with resin of 0.6 g and recycle tubular reactor with resin of 2.0 g and flow rates of 1.5 and 7.5 cm^3/min. The reaction rate of phosphazene-replaced reaction in a batch reactor was rapid than that in total recycle fixed-bed reaction. If the flow rate is increased, the efficiency of the sequential reaction is the same as that in a batch reactor. Because the mass-transfer resistance of the resin in fixed-bed reactor is larger than that in a batch reactor, the larger maximum yield of the monophenolated (diphenolated) product can easily be obtained when the flow rate is smaller, and on the other hand, the larger maximum yield of the third to sixth substituted product obtained as the flow rate is larger. Fig. 9 shows the performance of the recycle tubular reactor with the recycle ratio of 0 and ∞. Because the residence time of fixed-bed reactor was only 1.56 s, the reaction was not at steady state when the reaction time was more than 100 min (Fig. 9a). This finding also clarifies that the particle diffusion of reactant and product from the active site of resin to bulk solution influenced the reaction system.

4. Conclusions

The mass-transfer limitation of the reaction of hexachlorocyclotriphosphazene with phenol in a triphase reaction was investigated. The particle diffusion and intrinsic reactivity limit the organic reaction. However, if the role of organic solvent–aqueous solution in the resin cannot be clarified, the high efficiency of a novel catalyst cannot be developed. The mass-transfer resistances of the reactant and the product will still be barriers to apply this triphase technique from batch reactor to continuous process. In this study, after studying the effect of NaOH and particle size on the reaction, we offer the reaction mechanism and concept to hope this result can help the development of novel catalyst and continuous process.

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