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Catalytic Activity of Quaternary Ammonium Poly(methylstyrene-*co*-styrene) Resin in an Organic Solvent/Alkaline Solution

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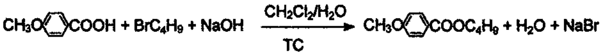
The reaction of 4-methoxyphenylacetic acid with *n*-bromobutane using triphase catalysis in a dichloromethane/alkaline solution was investigated. Meanwhile, the lab-produced resins and the commercial ion-exchange resin (triphase catalyst) were characterized in terms of the density of active sites, thermal stability, imbibed solvent composition, and reuse of the resin. The amount of active sites in the resin was characterized by EA, TGA, and Volhard methods. The imbibed amounts of organic solvent and water and the volume ratios for lab-produced resins were larger than those for commercial resins. The degradation of the catalyst due to temperature is greater than that due to base concentration. © **2001 Academic Press**

Key Words: **phase-transfer catalysis; triphase catalysis; catalytic activity; characterization; reuse.**

INTRODUCTION

Quaternary onium salts, crown ethers, cryptands, and polyethylene glycol have all been immobilized on various kinds of supports, including polymers (most commonly (methylstyrene-*co*-styrene) resin crosslinked with divinylbenzene), alumina, silica gel, clays, and zeolites (1–25). Because of diffusional limitations and high cost, the industrial applications of immobilized catalysis (triphase catalysis) are not fully utilized. This unfortunate lack of technology for industrial scale-up of triphase catalysis is mainly due to a lack of understanding of the complex interactions between the three phases involved in such a system. To date, there has been little literature discussion of the microenvironment. The effect of the internal molecular structure of the polymer support, which plays an important role in the imbibed composition, on the reaction rate has seldom been discussed. In addition to the reactivity, a triphase catalyst in an organic and aqueous solution must be selected with consideration of the volume swelling, imbibed different solvent ratio, amount of active site, and mechanical structure of catalyst. Hence, these complex interactions in the microenvironment must be determined in order to obtain a high reactivity of triphase catalyst.

Poly(styrene-*co*-chloromethylstyrene) crosslinked with divinylbenzene, which is immobilized with quaternary ammonium salts, was investigated to synthesize the fine chemicals in our previous works (26–30). The microenvironment of the polymer support played a crucial role in enhancing the reaction rate. More information about the characterization of the polymer structure, the interactions among organic solvent, resin, and aqueous solution, and the reuse of the catalyst is required to encourage application. Hence, in this study we aim to understand the microenvironment of the polymer support using instrumental analysis with TGA, EA, and reaction methods. The synthesis of 4-methoxybenzoic butyl ester (29) is shown in Eq. [1].



[1]

Twelve kinds of lab-produced quaternary ammonium resins and six kinds of commercial ion-exchange ammonium resins were investigated, as described in the following.

EXPERIMENTAL

Preparation of Triphase Catalyst

The procedure for the synthesis of polymer-supported phase-transfer catalyst (triphase catalyst) was identical to that in our previous works (27, 30). The procedure for the synthesis of the microporous resin was identical to that for macroporous resin, except that 4-methyl-2-pentanol was used as the pore-creating agent. The typical compositions of styrene, chloromethylstyrene, and divinylbenzene (crosslinking) in the resin were 76 wt%, 20 wt%, and 4 wt%, respectively. The particle sizes of the polymer pellet were determined by sieve analysis. Weight percents of microporous polymer collected were 20–40 mesh = 16%, 40–80 mesh = 31%, 80–120 mesh = 27%, 120–200 mesh = 19%, and 200–400 mesh = 7%.

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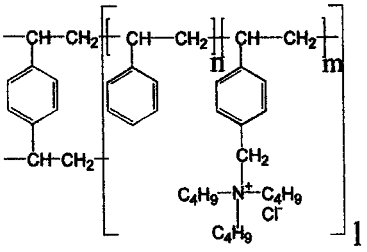
A 20.0 g amount of polymer pellets, 40 cm^3 of dimethylformamide, and 60.0 g of tri-*n*-butylamine were introduced into a 250-cm^3 flask at 60°C. The reaction mixture was agitated (400 rpm) for 6 days. The polymer was then filtered and washed with methanol, acetone, and anhydrous methanol, and dried under vacuum at 60°C.

The lab-produced resins were determined to be mi2-20, mi4-20, and ma2-20, etc. The notations "mi" and "ma" indicate microporous and macroporous, respectively. The first number is the percentage of crosslinking for divinylbenzene in the resin and the second is the percentage of ring substitution for chloromethylstyrene in the resin. The molecular structure of polymer-supported (styrene–chloromethylstyrene–divinylbenzene) resin is expressed as



Characterization of Resins

The procedure for determining the imbibed solvent composition of the resin is identical to that in Wang and Wu's 1992 report (28). 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. The external liquid phase was then 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.

Volume ratios ($V_R = \frac{\text{vol. of wet swollen resin}}{\text{vol. of dry resin}} = \sum_i (m_{si}/\rho_{si} + m_p/\rho_p)/m_p/\rho_p$) were calculated by assuming that the polymer density $\rho_p$was 1060 kg/m^3 (vs 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. m_p and m_{si} denote the masses of polymer and solvent, respectively, in the resin. Direct measurement of the porosity of the wet swollen resin was very difficult because of the solvent within the pores. The porosity of the wet swollen resin was thus estimated as $\varepsilon = 1 - 1/V_R$.

Kinetics of the Triphase Catalytic Reaction

For a kinetic run, an aliquot sample was withdrawn from the reaction solution at a selected time interval. 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 internal standard method.

RESULTS AND DISCUSSION

The content of tri-*n*-butylamine immobilized in the resin was determined by the TGA, EA, and Volhard methods. The solid and dashed lines, as shown in Fig. 1a, indicate the

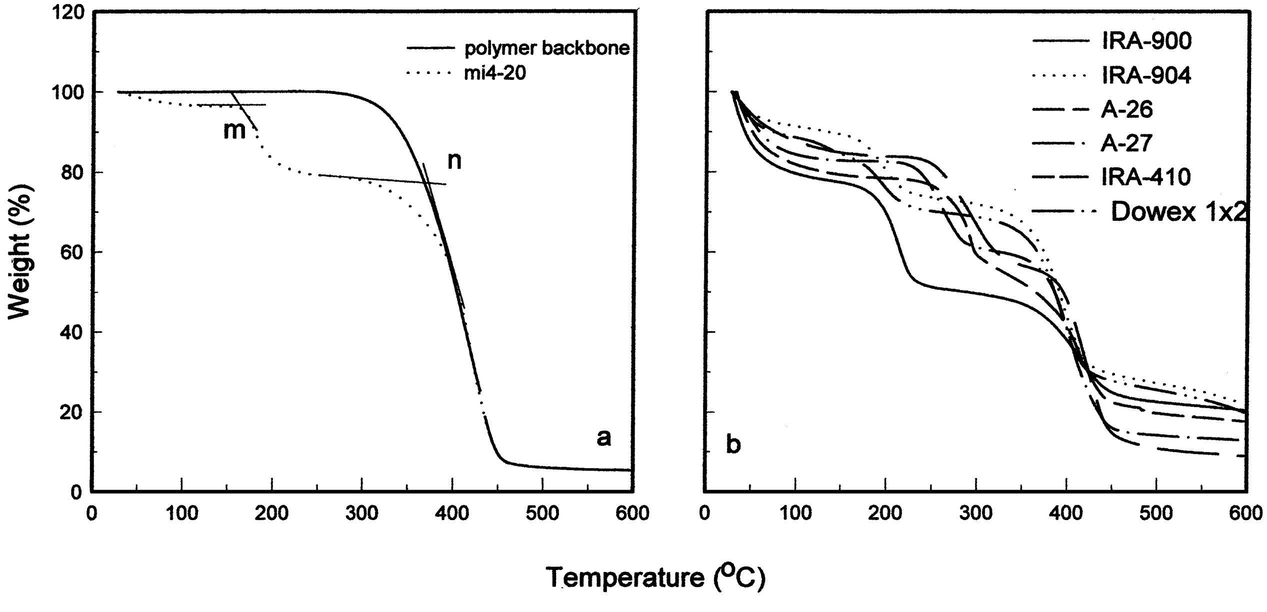


FIG. 1. Thermogravimetric curve of weight loss versus operating temperature for various resins.

thermal analysis of the resin mi4-20 of the polymer backbone and the polymer backbone with the functional group $-N(C_4H_9)_3$, respectively. The polymer backbone formed in a one-stage process where the decomposing temperature range was 300 to 450°C. The immobilized resin (mi4-20) was formed in a two-stage process, where the ranges of decomposition temperatures for the two stages were 160 to 200°C and 350 to 450°C. Although it is tempting to divide the two stages into two distinct units, the correlation between quaternary salt content and weight loss in the first step (weight at point m- weight at point n, as shown in Fig. 1a) was qualitative. The weight loss in the first step is equal to the amount of the immobilized functional group $-N(C_4H_9)_3$. The analytical technique was accurate to within 10%. The char yield at 600°C for TGA analysis of lab-produced resins was around 7%, which indicates the total amount of the metal salt in the resin. Figure 1b shows the TGA analysis of the commercial ion-exchange resin. These resins were revealed in a three-stage process. The decomposed compound and temperature for each decomposition step are imbibed water, ∼100°C; functional group, 160–300°C; and polymer backbone, 350–450°C. The sequence of the imbibed capability of water was IRA-900 (20%) > A-26 > Dowex 1 × 2 > A-27 ≈ IRA-410 > IRA-904 > mi4-20 (4%). Most commercial ion-exchange resins have a hydrophilic functional group. The decomposition temperatures of the functional groups of A26, IRA-410, and Dowex 1×2 (220–350°C) are larger than those of IRA-900, IRA-904, A27, and mi4-20 (160–220°C). The sequence of the char yield at 600°C for TGA analysis is IRA-904 (21%) > A-27 ≈ IRA-900 > A-26 > Dowex 1 × 2 > IRA-410 > mi4-20 (7%). This finding demonstrates that the salts in the resin synthesis process still remain in the resin. The resident salt will influence the utility of the resin in a triphase reaction, e.g., the imbibed solvent composition in the resin.

In addition, the amount of functional group $-N(C_4H_9)_3$ immobilized in the resin was determined from the mass fraction of nitrogen by elemental analysis (EA) for C, H, and N, from the weight loss at 160 to 200°C by TGA, and from the chloride ion density titrated by the Volhard method. Table 1 lists the content of tri-*n*-butylamine immobilized in the resin as determined by EA, TGA, and Volhard methods. The accuracy levels of our analytical techniques for TGA, EA, and Volhard methods were within 10%, 5%, and 3%, respectively. The sequence of the methods for the determination of the content of tri-*n*-butylamine immobilized in the resin was TGA > EA > Volhard, as shown in Table 1. The TGA (or EA) analysis was based on the elemental weight, and it reveals the real immobilized content. However, the Volhard method determined the amount of free chloride ion in the solution by the $AgNO_3$ titration method. The content of tri-*n*-butylamine immobilized in the resin as determined by the TGA (or EA) method was 20% larger than that determined by the Volhard method. The content of tri-*n*-butylamine immobilized in the resin as determined by the TGA (or EA) method was independent of the number of crosslinks, and only dependent of the number of the ring substitutions. The experimental results in Table 1 demonstrate the following:

TABLE 1

Amount of Functional Group ($-N(C_4H_9)_3Cl$) in the Resin

	Micro resin (mmol/g)			Macro resin (mmol/g)		
Resin	TGA	EA	Volhard	TGA	EA	Volhard
2-20	1.026	0.986	0.743	1.399	1.593	0.994
4-20	1.072	0.936	0.716	1.632	1.457	0.844
6-20	1.026	1.286	0.530	1.678	1.929	0.964
4-30	1.305	1.171	0.943	1.505	1.501	0.901
4-40	1.632	1.564	1.036	1.585	1.671	1.36
4-60	2.331	2.036	1.452	2.051	1.90	1.506

Note. The theoretical amount of functional group ($-N(C_4H_9)_3Cl$) in the resin of mi4-20 is 1.7 mmol/g.

(i) The percentage of the active site in the resins (number of ring substitutions) was smaller than that for addition of chloromethylstyrene to the polymer backbone for the synthesis (theoretical value). The theoretical ratio ($60/20 = 3$) of mi4-60 to mi4-20 was not equal to the immobilized content ($2.331/1.072 = 2.33$ for TGA) of mi4-60 to mi4-20.

(ii) In this study, tri-*n*-butylamine could be immobilized completely with the active site on the resin for an immobilized duration of 6 days. However, the content of immobilized tri-*n*-butylamine as determined by the Volhard method was dependent on both the number of crosslinks and the number of ring substitutions. The immobilized contents for the Volhard method are about 50–70% of that for TGA (or EA). Since the results of the Volhard analysis method determined the free chloride ions in the solution by the $AgNO_3$ titration method, the free chloride ions on the active site were measured at only 50–70% of the amount of immobilized content. The trend in the varied content for microresin is larger than that for macroresin. This result indicates that analysis by the Volhard method may be influenced by the diffusion problem. The results may be due to the fact that the resin had not swelled completely in the aqueous solution. On the other hand, if the resin is used as triphase catalyst to react in an actual reaction system, and the resin could not swell completely to release all free chloride ions, then the reaction environment would be influenced by the mass transfer of the reactant.

Figure 2 shows the amount of imbibed solvent, volume ratio, and porosity of 12 kinds of ion-exchange resins for seven kinds of solvents (dichloromethane, chloroform, 1,2-dichloroethane, benzene, toluene, chlorobenzene, and water) when 1 g of the resin was placed into 25 cm^3 of the pure solvent. The experimental results for the commercial ion-exchange resin are as follows. (i) The amounts

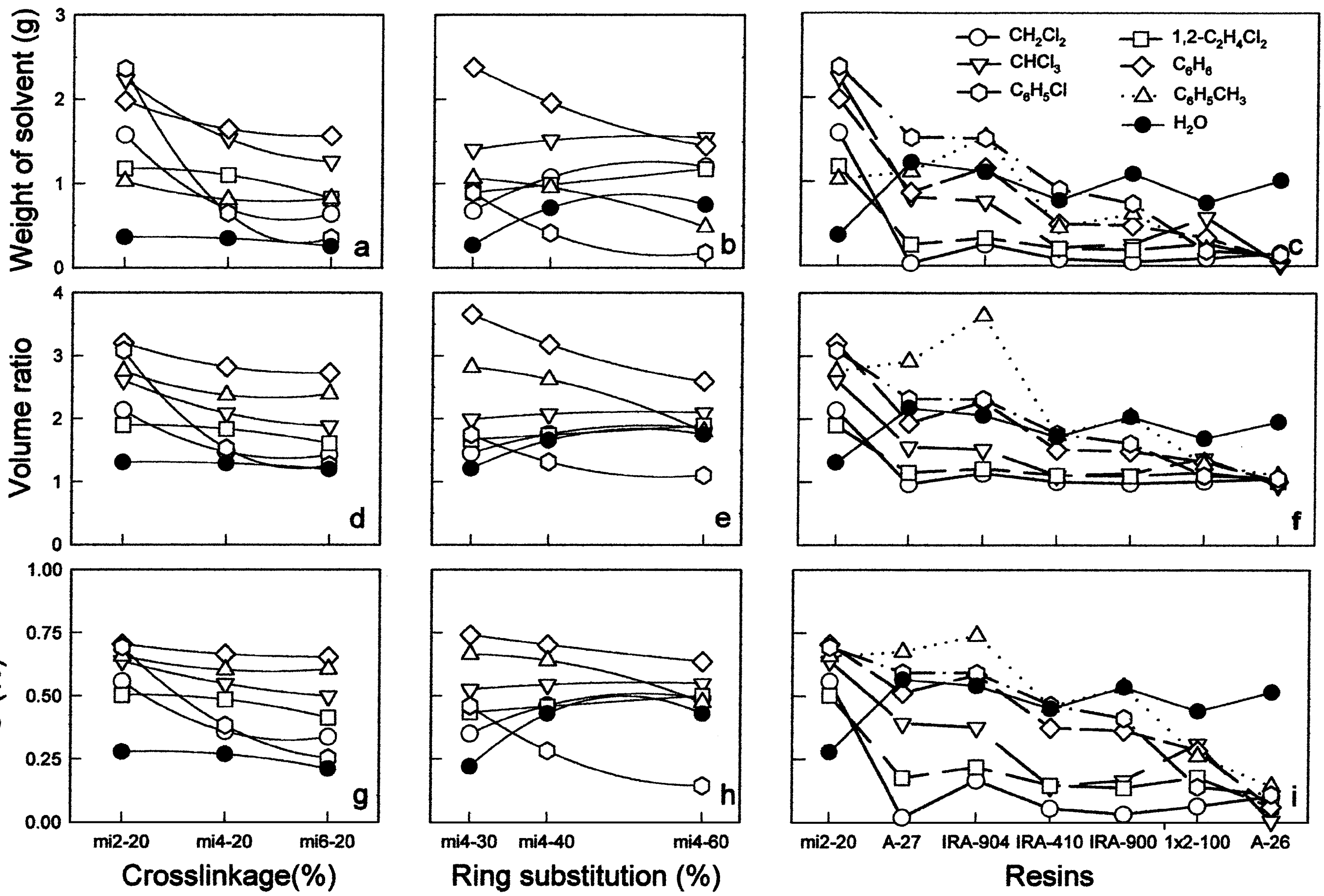


FIG. 2. Effect of solvent on the imbibed weight of solvent, volume ratio, and porosity for various resins in the chlorobenzene/water system: solvent = 25 cm^3, resin (45–60 mesh) = 1 g, 25°C.

of the imbibed solvent for the aromatic solvents (benzene, toluene, chlorobenzene) were larger than those for halide aliphatic solvents (dichloromethane, chloroform, 1,2-dichloroethane) since the resin was made from styrene. The sequence of the imbibed amount for the aromatic solvents is benzene > toluene > chlorobenzene. (ii) The imbibed amounts for water and organic solvent were around 1 g and less than 1 g, respectively. (iii) The volume ratios were between 1 and 2. (iv) The porosities were between 0.5 and 0. The porosity of the ion-exchange resin was about 0.5 (31).

The experimental results for the lab-produced resins are as follows. (i) The amounts of the imbibed solvent were dependent on the structure of the resins. The amount of imbibed solvent for water was smaller than that for organic solvent. (ii) The amounts of imbibed solvent were in the range of 0 to 3. (iii) The volume ratios were almost all between 1 and 3. The volume ratio decreased with increasing crosslinking of the resin. (iv) The porosities were between 0.25 and 0.75. The porosity and imbibed amount decreased for the solvents benzene, toluene, and chlorobenzene, and increased for the solvents chloroform, 1,2-dichloroethane, dichloromethane, and water, with increasing number of ring substitution. These results indicate that the solubility of water in chloroform, 1,2-dichloroethane, and dichloromethane is larger than the solubility in benzene, toluene, and chlorobenzene. The imbibed amount for aromatic solvents was larger than that for halide aliphatic solvents when the number of ring substitutions was small, and the trend was opposite when the number of ring substitutions was large.

Because the functional group (tetra-*n*-butylammonium chloride) of the lab-produced resin is more lipophilic than that (tetramethyl(or ethyl)ammonium chloride) of the commercial ion-exchange resin, the amount of imbibed water was larger than that of the organic solvent for the commercial resin, and in contrast, for the lab-produced resin, the amount of water was less than that of organic solvent. The imbibed amount of organic solvent for the lab-produced resin was larger than that for the commercial resin, as shown from the ε values in Fig. 2. Although the swollen volumes of A-27 and IRA-904 were high in the

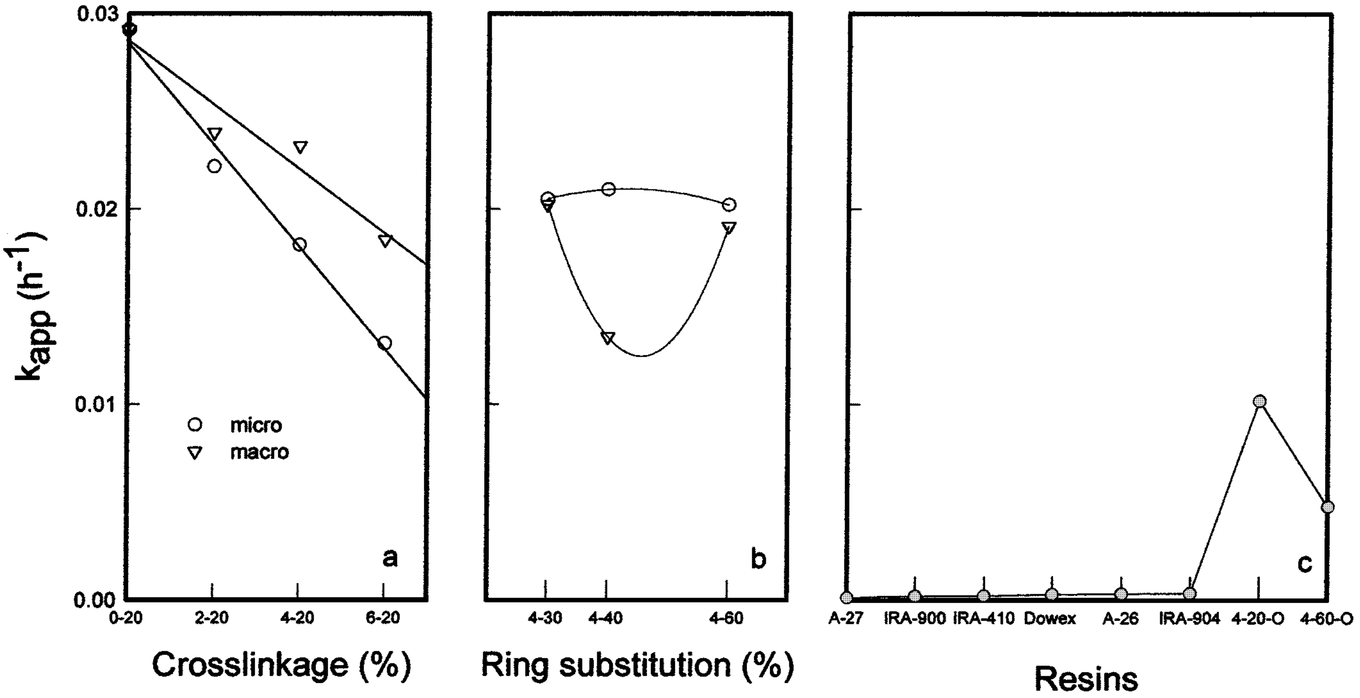


FIG. 3. Plot of apparent reaction rate constant for various resins: 1000 rpm, resin = 1.5 g, KOH (7 kmol/m^3) = 50 cm^3,$CH_3OC_6H_4CH_2COOH$ = 0.03 mol, 1-Br(C_4H_9) = 0.073 mol, 55°C.

commercial resin, the others were not good for swelling. Hence, the commercial resins are not suitable for use as phase-transfer catalyst in an organic phase/aqueous solution reaction system.

Reaction of 4-Methoxyphenylacetic Acid with n-Bromobutane

The rate of the triphase reaction is controlled by many factors, including the reactivity of the active site, degree of crosslinking, degree of swelling, number of ring substitutions, particle size, temperature, and imbibed solvent composition in the resin. Hence, the reaction of 4- methoxybenzoic butyl ester with 4-methoxyphenylacetic acid and *n*-bromobutane using triphase catalysis investigated by our previous work (29) was chosen as a model reaction to understand the relationship between the reaction phenomenon and the structure of the resin. The reaction rate for the organic phase follows pseudo-first-order kinetics and can be written as

$$\begin{aligned}-r_{BrC_4H_9} &= r_{CH_3OC_6H_5COOC_4H_9}\\ &= k_{BrC_4H_9}[\text{resin}^+CH_3OC_6H_4COO^-][\overline{BrC_4H_9}]\\ &= k_{f,app}[\overline{BrC_4H_9}],\end{aligned} \qquad [2]$$

where $k_{f,app}$ is the apparent reaction rate constant for formation of 4-methoxybenzoic butyl ester. The effects of temperature, base, structure,and reuse of the resin are discussed in the following.

Figure 3 shows the effects of the degree of crosslinking, the number of ring substitutions, and various kinds of resins on the reactivity of the 4-methoxybenzoic butyl ester reacting with 4-methoxyphenylacetic acid and *n*-bromobutane using triphase catalysis. Increasing the degree of crosslinking for both the micro resin and the macro resin decreased the apparent reaction rate constant, and the reactivity for the macro resin was larger than that for the micro resin (Fig. 3a). The apparent reaction rate constant remained constant for the micro resin and had a minimum value for the macro-resin with increasing number of ring substitutions, and the reactivity for the macro resin was smaller than that for the micro resin (Fig. 3b). The reactivity for six commercial ion-exchange resins was very low (Fig. 3c). According to the results in Fig. 2, the functional group of the commercial resins was a hydrophilic group (tetramethyl(or ethyl)ammonium); in fact, the imbibed solvent ratio of organic solvent to water was small. The imbibed solvent ratio and hydrophobicity of the resin were increased with increasing carbon number in the alkyl group. Figure 3c shows the reactivity for two resins (4-20-O and 4-60-O) for which the functional group is the tetra-*n*-octylammonium group. The reactivity for tetra-*n*-octylammonium was also smaller than that for the tetrabutylammonium group. Hence, the excessive hydrophilicity or lipophilicity of the functional group is not of use in the triphase catalytic reaction.

In general, the reaction rate increases with augmentation of the polarity of the solvent. In this study, five

TABLE 2

Activation Energies for the Reaction of 4-Methoxyphenylacetic Acid with *n*-Bromobutane in Various Solvents

	E_a (kcal/mol)				
	C_6H_5Cl	C_6H_6	$C_6H_5CH_3$	CH_2Cl_2	$CHCl_3$
Micro resin	15.8	17.1	19.9	15.8	12.1
Macro resin	14.1	14.3	14.6	13.0	13.0

Conditions. 1000 rpm, resin = 1.5 g, KOH (7 kmol/m^3) = 50 cm^3, $CH_3OC_6H_4CH_2COOH$ = 0.03 mol, 1-Br(C_4H_9) = 0.073 mol.

kinds of solvents with various polarities were used as the organic solvents in the triphase catalytic reaction. The sequence of the reactivity for the macro resin was $CH_2Cl_2 > CHCl_3 > C_6H_5Cl > C_6H_6 > C_6H_5CH_3$, and the trend for the micro resin was similar, except for chloroform. The increment of the reactivity of this triphase reaction corresponds to the polarity of solvent. Dichloromethane had the highest reactivity among the solvents. However, the boiling point of dichloromethane is 39°C, and it is impractical for reaction in the higher temperature reaction system. Table 2 lists the Arrhenius activity energy for various solvents. The activity energy varied with the structure of the resin. Most activity energy levels for micro resins were larger than those for macro resins, except for chloroform.

The four functions of a base in a liquid–solid–liquid triphase catalytic reaction were reported in our previous work (Wu and Meng, 1999) (30): (i) as a reactant; (ii) in deprotonation of the acidic organic compound to become the reactive form; (iii) for improving the reactive environment in the catalytic pellets, such as swelling volume, imbibed composition, solubility between two phases, etc.; and (iv) for reducing the solvation of catalyst and water to upgrade the reactivity of active catalyst in the organic phase. Figure 4 shows the effect of base concentration for the reactivity of 4-methoxyphenylacetic acid. The apparent reaction rate constant was almost constant when the NaOH (or KOH) concentration was larger than 1 kmol/m^3. The increment of the deprotonation of 4-methoxyphenylacetic acid dramatically increased the reactivity of the reaction when the base concentration was below 1 kmol/m^3. When the salt concentration was increased to change the reaction environment, the reactivity of the reaction was slightly increased with increasing base concentration. The reactivity for KOH was larger than that for NaOH.

The advantages of using triphase catalytic reaction are that it easily recovers the catalyst and purifies the product and reactant. Hence, the reuse, stability, and degradation of the catalyst must always be considered. Resins with onium groups may be used for extended periods or repeated cycles only if the catalyzed reactions occur under sufficiently mild conditions to avoid degradation. The

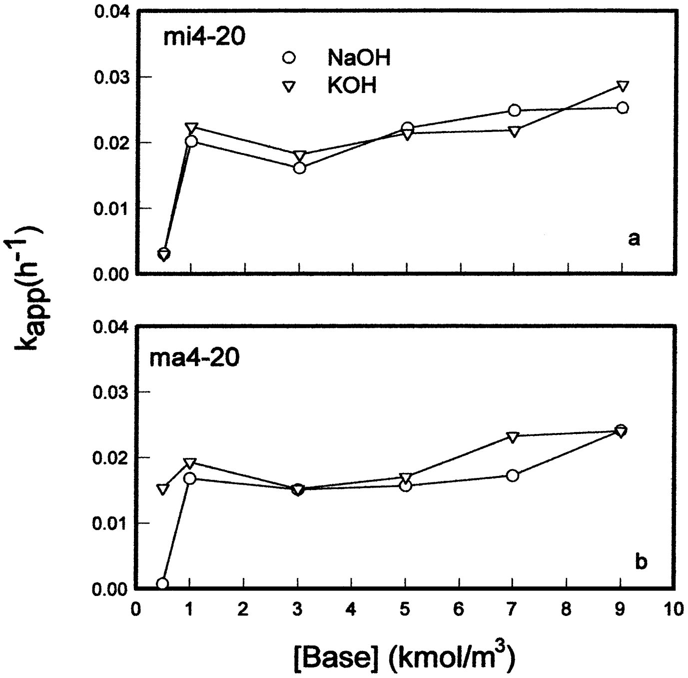


FIG. 4. Effect of base concentration on apparent reaction rate constant for various resins: 1000 rpm, resin = 1.5 g, base solution = 50 cm^3, $CH_3OC_6H_4CH_2COOH$ = 0.03 mol, 1-Br(C_4H_9) = 0.073 mol, 55°C.

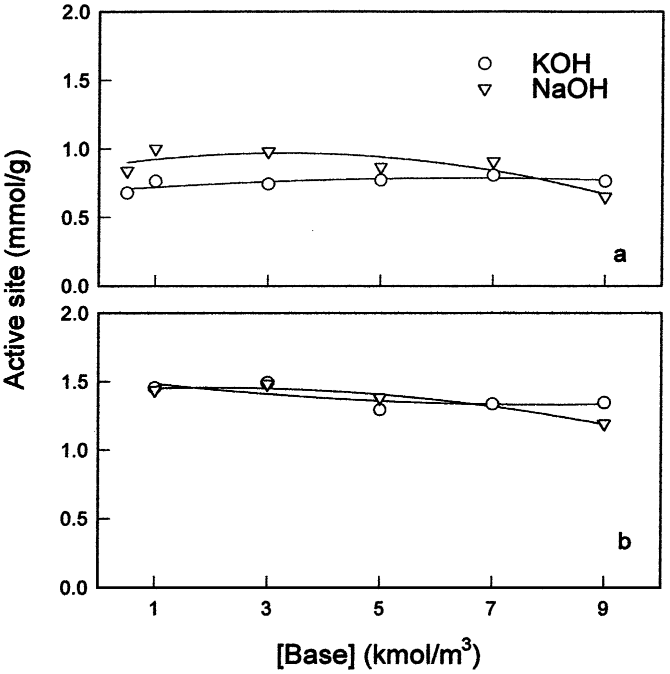


FIG. 5. Effect of base concentration on the amount of active site in the resin determined by elemental analysis after 5 h for the formation of 4-methoxyphenoxyacetic acid butyl ester: 1000 rpm, resin (45–60 mesh) = 1.5 g, base solution = 50 cm^3, $CH_3OC_6H_4CH_2COOH = 0.03$ mol, 1-Br(C_4H_9) = 0.073 mol, 55°C. (a) Microporous resin; (b) macroporous resin.

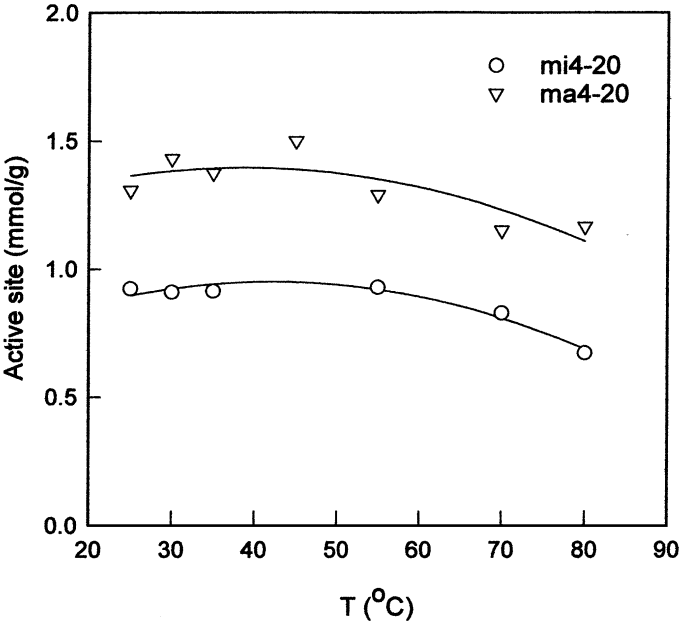


FIG. 6. Effect of temperature on the amount of active site in the resin determined by elemental analysis after 5 h for the formation of 4-methoxyphenoxyacetic acid butyl ester: 1000 rpm, resin (45–60 mesh) = 1.5 g, KOH (7 kmol/m^3) = 50 cm^3, $CH_3OC_6H_4CH_2COOH$ = 0.03 mol, 1-Br(C_4H_9) = 0.073 mol.

degradation of the triphase catalyst may be due to three factors: high temperature, strong base, and mechanical degradation. In the past literature (14, 15, 32–35), the reactivity of the triphase reaction was influenced slightly by the degradation of the catalyst (polymer-supported resin). From Figs. 5 and 6, the active site is seen to decrease slightly with increasing base concentration up to 9 kmol/m^3 (Fig. 5). The number of active sites remained constant up to 60°C, and then decreased dramatically as the temperature increased (Fig. 6). The degradation of the catalyst with temperature is more extreme than that with base concentration.

CONCLUSIONS

The amount of active sites in the resin was characterized by EA, TGA, and Volhard methods. The accuracy of analyzing active sites by EA was the best of the three methods, followed by the TGA method. In addition, the TGA data can indicate the amount of the functional group type and the resident metal salt in the resin. The amount of active sites determined by using the Volhard method was low because of the diffusion problem with chloride ion. However, this phenomenon may correspond to that in an actual reaction system. The increment of the reactivity of this triphase reaction corresponds to the polarity of solvent and the base concentration. The degradation of the catalyst with temperature is greater than that with base concentration. The degradation of the catalyst dramatically increased when the temperature was higher than 60°C.

ACKNOWLEDGMENTS

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