1246 *Macromolecules* 1982, *15*, 1246-1251

Mechanisms of Polymer-Supported Catalysis. 3. Ion Exchange Limitations and Macroporous Polystyrene Supports

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Received February 16, 1982

ABSTRACT: Rates of reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by insoluble polystyrene-supported benzyltri-*n*-butylphosphonium ions were determined for both macroporous and nonmacroporous polymers. The macroporous supports gave slightly slower rates in spite of their greater porosities and surface areas. Rates decreased as the degree of cross-linking of the macroporous polymers increased from 2% to 75% divinylbenzene. Catalysts recovered from reaction mixtures contained more bromide ion than cyanide ion. Possible reasons for the retention of bromide ion in the catalysts and the low activity of the macroporous catalysts are discussed.

Insoluble polymer-supported phase-transfer catalysts can be separated easily from reaction mixtures by filtration and reused. Polymer-supported quaternary ammonium and phosphonium ions, crown ethers, and cryptands catalyze numerous organic reactions, of which the most common are nucleophilic displacements.[2] However, the catalytic activities of the polymer-supported catalysts often are less than those of the analogous soluble phase-transfer catalysts because reaction rates are limited by diffusional processes. An investigation of the effects of polymer cross-linking, particle size, and method of mixing on the rate of reaction of aqueous sodium cyanide with organic solutions of 1-bromooctane catalyzed by polystyrene-bound benzyltri-*n*-butylphosphonium ions (eq 1) showed that

$$n\text{-}C_8H_{17}Br + NaCN(aq) \rightarrow n\text{-}C_8H_{17}CN + NaBr(aq) \quad (1)$$

$$\text{catalyst: polystyryl–}CH_2P(n\text{-}C_4H_9)_3{}^+Cl^-$$

mass transfer of reactant from bulk liquid phase to the particle surface limited rates unless vigorous stirring was employed and that intraparticle diffusion partially limited the rates under almost all conditions employed.[3] The intrinsic reaction rate at the active sites is the other limiting factor. The evidence for intraparticle diffusional limitation is that the rate of the triphase reaction increases as the particle size of the catalyst decreases and as the degree of cross-linking of the polystyrene decreases: the smaller the particle, the shorter the diffusion path from the particle surface to a catalytic site; the more highly cross-linked the polymer, the more tortuous the diffusion path. In the case of reaction of cyanide ion with 1-bromooctane, transport of either the alkyl halide or the cyanide ion from bulk liquid phases into the polymer or transport of either the alkyl cyanide or the bromide ion out of the polymer could limit observed rates.

Because of these diffusional limitations we have investigated the activities of benzyltri-*n*-butylphosphonium ion catalysts bound to macroporous polystyrene supports. A macroporous polymer is porous even in dry form. The polystyrene particles used in most investigations of polymer-supported catalysts are microporous; they become porous only as they swell in good solvents. The micropores are the liquid-filled spaces between polymer chains in the network. In swelling solvents macroporous polymers have both macropores and micropores. The swollen macropore structure is related to the pore structure of the dry polymer, and the microporosity should be similar to that of a nonmacroporous polymer that has the same degree of cross-linking. Transport of a reactant molecule or ion from the outer surface of a macroporous particle to a catalytic site may proceed mainly through the liquid-filled macropores. This leaves only a short diffusion path from the internal surface of a macropore through the microporous polymer matrix to the active site. The microparticles that comprise the polymer bead have dimensions more than 2 orders of magnitude smaller than the macroparticle. Consequently, if intraparticle diffusion limits the rates of phase-transfer-catalyzed reactions, the rates may be faster with a macroporous catalyst.

Table I
Phosphonium Salt Formation in 50% and 75% Cross-Linked Polymers

% cross-linking	solvent	*T*, °C	mequiv of Cl^-/g[a]
50	1,2-dichloropropane	96	0.13
75			0.14
50	*m*-xylene	138	0.13
75			0.11
50	*o*-dichlorobenzene[b]	180	0.32
75			0.19

[a] Calculated value for complete phosphonium ion formation is 0.58 mequiv/g. [b] Tri-*n*-butylphosphine (5.0 molar equiv) was used. Other experiments used 1.5 molar equiv of tri-*n*-butylphosphine.

Regen, Bolikal, and Barcelon[5] reported that macroporous polystyrene-bound benzyltri-*n*-butylphosphonium ion catalysts were no more active than nonmacroporous catalysts for reaction of *n*-decyl methanesulfonate with aqueous sodium chloride. Their "macroporous" catalysts had BET nitrogen adsorption surface areas of < 1 m^2/g. Our study of macroporous polystyrene supports for phase-transfer catalysis started before we were aware of Regen's results.[5] We, too, have observed no improvement in catalytic activity by use of macroporous polymer supports, and we have carried out further experiments to try to understand why.

Experimental Section

Polymer Syntheses. The microporous copolymers of styrene, divinylbenzene (55% technical, Polysciences), and (chloromethyl)styrene (Dow vinylbenzyl chloride, 60/40 m/p) were prepared as described before.[3] The 50% and 75% cross-linked polymers were prepared with 83% active divinylbenzene. Macroporous suspension copolymers were prepared by the same method except that the monomer phase contained 45% by weight 4-methyl-2-pentanol (Aldrich), which was removed from the polymer by steam distillation after polymerization was complete.

Catalysts were prepared by heating the copolymer beads with 1.5 molar equiv of tri-*n*-butylphosphine (Aldrich) under nitrogen with stirring in refluxing 1,2-dichloropropane. After thorough washing with methanol, acetone, and methanol and drying under vacuum at 60 °C, the chloride content was determined by a Volhard titration.[3] The 50% and 75% cross-linked copolymers

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Table II
Properties and Kinetic Activities of Macroporous Catalysts

% cross-linking[a]	% CMS[a]	mesh size	% ring subst	$10^5 k_{\mathrm{obsd}}$, s^{-1}	surface area, m^2/g[e]	bulk density, g/mL
2	25	100/200	15	13.7	1.1	0.32
4	25	100/200	14	13.9	9.7	0.31
6	25	100/200	12	8.8	17.1	0.28
10	25	100/200	11	5.6	25.4	0.28
20	25	200/400	8	1.35		
20[b]	50[b]	200/400	15	6.3[f]	19.4	
20[b]	50[b]	200/400	49[c]	0.32		
20[b]	50[b]	200/400	15 + 9.5[d]	3.4		
20[b]	75[b]	200/400	28	4.0[g]		
50	10	40/60	3	0.16		
75	10	40/60	3	0.08	588	
7	87	30/40	61	1.40		
Amberlyst A-27[h]		20/40	40[c]	<0.01	46.9	0.33
2[i]	25	100/200	0	<0.01		

[a] Weight percent divinylbenzene and weight percent (chloromethyl)styrenes in copolymer unless noted otherwise. [b] Mole percent. [c] Benzyltrimethylammonium ion. [d] 15% Benzyltri-*n*-butylphosphonium ion and 9.5% benzyltrimethylammonium ion. [e] Determined by the one-point BET nitrogen adsorption method. [f] Average of two runs: ±0.3. [g] Average of two runs: ±0.3. [h] Rohm and Haas Co. Surface area and bulk density are from: Kun, K. A.; Kunin, R. *J. Polym. Sci., Part C* **1967**, *16*, 1457-1469. [i] Control experiment with copolymer, 2% divinylbenzene, and 25% (chloromethyl)styrenes by weight.

gave only low conversion to phosphonium salts under these conditions, so higher boiling swelling solvents, *m*-xylene and *o*-dichlorobenzene, were used at reflux. Only slightly higher degrees of functionalization were attained (see Table I).

Some of the copolymers and phosphonium salt catalysts were washed with acetone and methanol, dried under vacuum at 60 °C, and analyzed for surface area by the one-point BET nitrogen adsorption method.[6] Bulk densities of the macroporous catalysts were determined by weighing 4.0 mL of the polymer in a calibrated graduated cylinder. The analogous 2% and 10% cross-linked gel polymeric catalysts had bulk densities of 0.65 and 0.64 g/mL. The surface area and bulk density data are in Table II.

Scanning electron micrographs were taken with a JEOL JSM 35U instrument at 25-kV accelerating voltage. Samples were coated with 100 Å of Au/Pd with a Hummer II instrument.

Kinetics were performed as described before.[3] All runs used 2.0 mol % catalyst. All runs included 5 or 6 data points. All runs except those with $k_{\mathrm{obsd}} < 1 \times 10^{-5}\ s^{-1}$ were carried to 13-60% conversion at the last data point. Rate constants are averages of the 4 or 5 values calculated from eq 2, in which n and $n + 1$

$$k = (t_{n+1} - t_n)^{-1} \ln ([\mathrm{RBr}]_n/[\mathrm{RBr}]_{n+1}) \qquad (2)$$

represent successive data points. Each run was preceded by stirring the catalyst for 60 min at 90 °C with all components of the reaction mixture except 1-bromooctane.

Bromide and Cyanide Contents of Recovered Catalysts. Each experiment was performed exactly as a kinetic run to the degree of conversion shown in Table III. To provide larger samples for analysis, 4 mol % catalyst was used. The organic phase was analyzed for 1-bromooctane and 1-cyanooctane by gas chromatography to establish percent conversion. The reaction mixture was removed from the 90 °C bath and filtered at room temperature through a medium-porosity fritted glass funnel (Corning Glass Co.). The recovered catalyst was washed with 100 mL of nitrogen-purged methanol for 30 min and 100 mL of nitrogen-purged water for 30 min. The catalyst sample was divided into two equal parts. The first was soaked in 10 mL of *N,N*-dimethylformamide for 2 h, and 20 mL of 3 N aqueous sodium nitrate was added. After 10 h the liquid was drained, and the sample was washed with 100 mL of 3 N aqueous sodium nitrate over a period of 40 min. The pH of the combined filtrate was reduced to 1–2 with 6 N nitric acid, and the solution was purged with a stream of nitrogen to remove the liberated HCN (in a fume hood!). The bromide content of the filtrate was determined by Volhard titration. The solid catalyst was washed further with 150 mL of methanol and dried under vacuum at 60 °C. The dry weight was used to calculate mequiv of Br^-/g of recovered catalyst.

The second half of recovered, water-washed catalyst was returned to a fresh reaction mixture, the same as that used for kinetic runs except that its aqueous phase contained no sodium cyanide, and an accurately weighed 1.0-g portion of 1-bromooctane was used. The mixture was stirred at 90 °C for >24 h to ensure complete conversion of the cyanide ion in the catalyst to 1-cyanooctane. The organic phase was analyzed by gas chromatography for 1-bromooctane and 1-cyanooctane, and the millimoles of 1-cyanooctane formed were calculated from the calibrated relative peak areas and the weight of 1-bromooctane used. The catalyst recovered from this second reaction was washed thoroughly with methanol and dried. Its dry weight and the millimoles of 1-cyanooctane produced establish mequiv of CN^-/g in the recovered catalyst.

Table III
Bromide and Cyanide Contents of Recovered Catalysts

% cross-linking[a]	catalyst porosity	mequiv of Cl^-/g[b]	% conv	mequiv of Br^-/g[c]	mequiv of CN^-/g[c]
2	micro	1.12	57[d]	0.49	0.29
4	micro	1.15	60	0.60	0.29
6	micro	1.12	74	0.72	0.28
10	micro	1.04	86	0.63	0.18
2	macro	1.03	47	0.40	0.61
4	macro	1.01	50	0.52	0.37
6	macro	0.92	41[e]	0.48	0.47
10	macro	0.65	36	0.34	0.24
20[f]	macro	1.03	65	0.55	0.19
2	micro	1.12	0	0.29[g]	0.56[g]

[a] Weight percent divinylbenzene in (chloromethyl)styrene copolymer. [b] In starting catalyst. [c] In recovered catalyst. [d] Average of three experiments. Deviations were ±4% conversion and ±0.04 mequiv/g. [e] Average of two experiments. Deviations were ±6% conversion, ±0.03 mequiv/g of Br^-, and ±0.01 mequiv/g of CN^-. [f] Mole percent divinylbenzene. [g] Average of two experiments. Deviations were ±0.03 mequiv/g of Cl^- and ±0.01 mequiv/g of CN^-.

In some experiments the percent of active sites remaining in the recovered catalyst was determined by conversion of the catalyst back to its original chloride form. The catalyst was soaked 6 h in a mixture of 17 mL of concentrated aqueous HCl and 155 mL of methanol and washed with methanol. The catalyst was dried and analyzed for chloride by the usual titrimetric method.

Although results in duplicate and triplicate experiments in Table III suggest greater precision, our level of confidence in the bromide analyses is ±0.05 mequiv/g and in the cyanide analyses ±0.10 mequiv/g because of the required detection of a small amount of 1-cyanooctane relative to a large amount of 1-bromooctane.

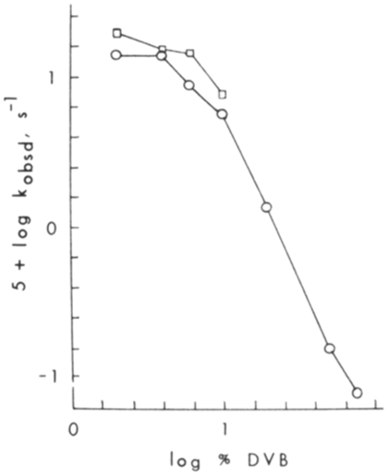

Figure 1. Dependence of k_{obsd} on percent cross-linker for nonmacroporous (□) and macroporous (○) catalysts.

Equilibration of Br^- and CN^- with Catalysts. A 0.243-g (0.250 mequiv) sample of the 2% cross-linked macroporous catalyst was swollen in 5 mL of toluene in a test tube for 1 h. A solution of 0.1155 g (2.36 mequiv) of sodium cyanide in 0.400 mL of water (the same concentration of NaCN used in kinetic experiments) was added. The mixture was stirred magnetically and heated to 90 °C for 2.5 h. The mixture was filtered, and the catalyst was washed with 75 mL each of methanol and water. Bromide content of the catalyst was analyzed as 0.138 mequiv/g by the method used with catalysts recovered from kinetic experiments. These data and eq 3,[7] in which $\bar{\chi}_{Br}$ and $\bar{\chi}_{CN}$ are molar

$$K_{CN}^{Br} = \bar{\chi}_{Br}\chi_{CN}/\bar{\chi}_{CN}\chi_{Br} \qquad (3)$$

quantities inside the particles and χ_{BR} and χ_{CN} are molar quantities in the external aqueous phase, give a selectivity coefficient $K_{CN}^{Br} = 1.52$. A similar experiment with the 10% cross-linked macroporous catalyst gave $K_{CN}^{Br} = 2.85$.

Results

Rates of displacement of bromide ion from 1-bromooctane in toluene by a tenfold excess of aqueous sodium cyanide catalyzed by polystyrene-supported benzyltri-*n*-butylphosphonium ions are reported in Table II and plotted as a function of weight percent divinylbenzene cross-linking of the polymer in Figure 1. All experiments were performed with 400–440-rpm mechanical stirring, shown previously to overcome mass transfer limitations on the rates of the catalyzed reactions.[3] With both the macroporous and the nonmacroporous supports, reaction rates decreased as the degree of cross-linking of the polymer increased. With the high surface area 50% and 75% cross-linked catalysts, the reaction rates were extremely low, but still more than 8 times faster than in control experiments (last line of Table II) in which no polymer beads or 2% cross-linked polymer beads containing only chloromethyl groups were used. The rates of reactions with macroporous catalysts were lower than those with nonmacroporous catalysts having the same degree of cross-linking, although the rate constants with the two 4% cross-linked catalysts were within experimental error of one another. The commercial ion exchange resin catalyst Amberlyst A-27 was completely inactive under triphase conditions.

Since the intrinsic reactivity of cyanide ion and 1-bromooctane should depend only on the environment at the active site within the polymer network and macroporosity should not affect the active-site environment if there is no change in degree of cross-linking, the lower activities of the higher surface area macroporous catalysts must be due to their failure to increase the rate of transport of reactants to the active sites. There could be slow transport of either the ions (cyanide in and bromide out) or the

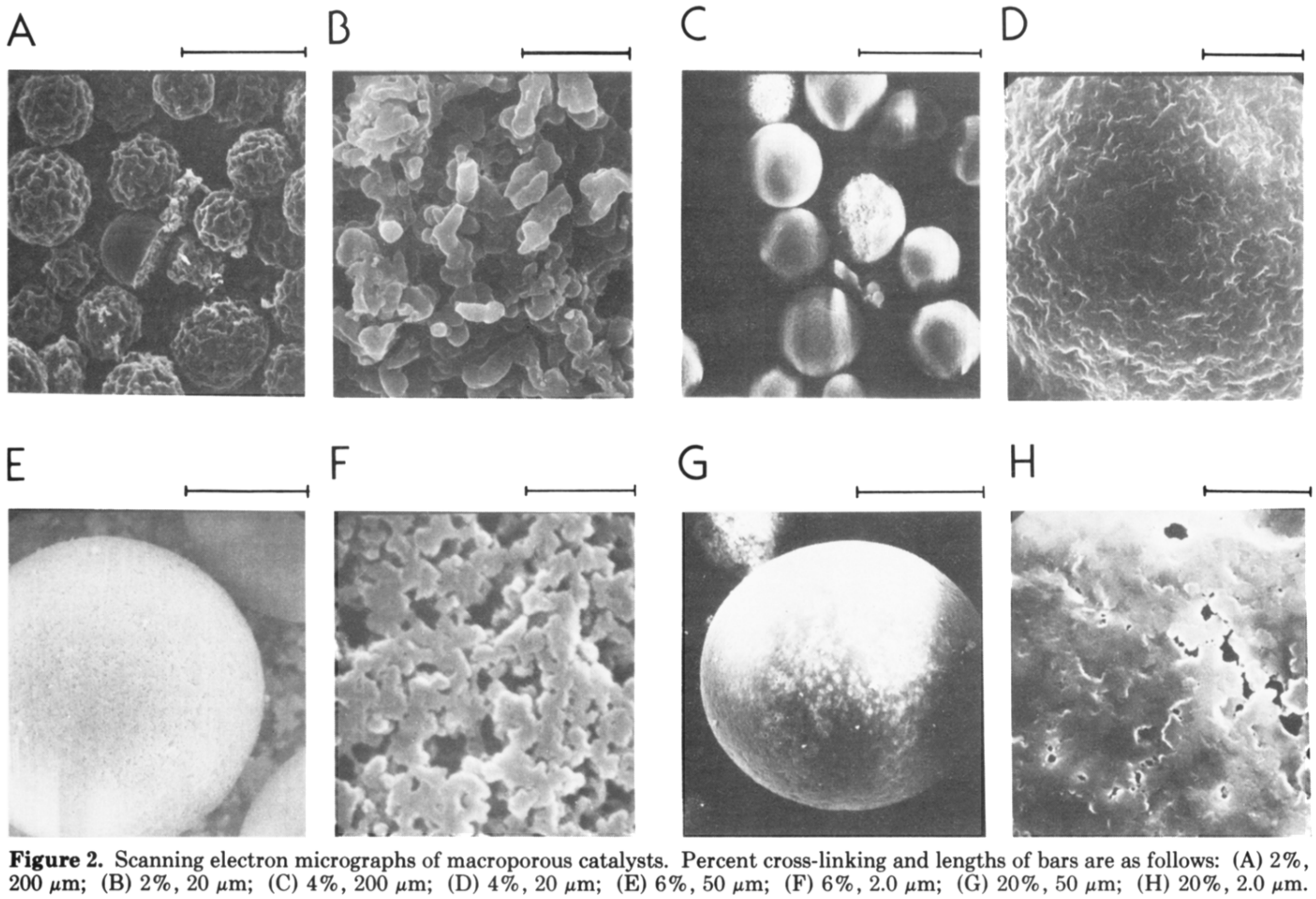

Figure 2. Scanning electron micrographs of macroporous catalysts. Percent cross-linking and lengths of bars are as follows: (A) 2%, 200 μm; (B) 2%, 20 μm; (C) 4%, 200 μm; (D) 4%, 20 μm; (E) 6%, 50 μm; (F) 6%, 2.0 μm; (G) 20%, 50 μm; (H) 20%, 2.0 μm.

neutral organic molecules (1-bromooctane in and 1-cyanooctane out).

The scanning electron micrographs in Figure 2 show clearly the macroporous nature of the 2% and 6% cross-linked catalysts. However, the 4% and 20% cross-linked catalysts (and the 10%, 50%, and 75% cross-linked macroporous catalysts not shown) have relatively smooth surfaces punctured only by occasional holes. Since the bulk densities of the macroporous catalysts are half those of the nonmacroporous catalysts and since they have substantial surface areas, there is no doubt about their macroporous nature. The 4% and 20% cross-linked samples must have a thin skin of polymer on the particle surface hiding the macropores. One might predict that the skin of polymer on the surface could retard transport of reactants into the 4% cross-linked catalyst and reduce its activity compared with the 2% and 6% cross-linked catalysts. Data in Table II and Figure 1 disprove that prediction; the 4% and 2% cross-linked macroporous catalysts have the same activity.

A possible reason for slow transport in the macroporous catalysts is that either the aqueous phase or the organic phase fails to penetrate the macropores. Every kinetic run was preceded by 60-min conditioning at 90 °C with stirring in the presence of all components of the reaction mixture except 1-bromooctane. We reasoned that initial filling of the macropores with a water-miscible solvent or degassing the catalyst in the presence of water might promote penetration of the macropores by the aqueous phase. Experiments were conducted with the 20% cross-linked, 15% ring-substituted catalyst (Table II) in which the catalyst was (1) swollen in tetrahydrofuran (THF) before use, (2) swollen in THF and rinsed with water, (3) swollen in 1,4-dioxane and rinsed with water, (4) degassed in the presence of only the aqueous phase, and (5) degassed in toluene only. Degassing in toluene resulted in a rate constant the same as that in Table II. All of the attempts to fill the macropores with aqueous phase before the kinetic run resulted in rate constants of $<1.0 \times 10^{-5}$ s^{-1}, less than one-sixth as fast as in the conventional kinetic runs.

The kinetic experiments were run with a tenfold excess of cyanide ion over 1-bromooctane, with the intent of making cyanide transport fast. To determine the extent of ion exchange during kinetic runs, reaction mixtures after partial conversion of 1-bromooctane to 1-cyanooctane were taken from the 90 °C bath and poured quickly through a fritted funnel at room temperature. The ion contents of recovered catalysts are in Table III. The catalysts contained much more bromide than cyanide after 9–22 turnovers per active site (35–86% conversion using 4 mol % catalyst). Since not all sites were equally active, the turnover numbers must have been higher at the most active sites, which were likely nearest the particle surface. The macroporous catalysts retained slightly less bromide ion than the nonmacroporous catalysts. Also, as the percent divinylbenzene in the polymer increased, there was a higher ratio of bromide to cyanide in the recovered catalysts. Even after 60-min conditioning in toluene and aqueous sodium cyanide, the 2% cross-linked gel catalyst retained 29% of its original chloride ion, indicating that at least 29% of the phosphonium ion sites were catalytically inactive.

The ion analyses in Table III also provide a determination of the number of ion exchange sites remaining in each sample. Although experimental errors in the sum of bromide and cyanide detected may be ±0.15 mequiv/g (see Experimental Section), the catalysts clearly lost active sites during use. The extent of loss of ion exchange sites did not depend on the percent divinylbenzene cross-linking or on macroporosity.

Attempts were made to determine the toluene, 1-bromooctane, and 1-cyanooctane contents of the catalysts under reaction conditions at 90 °C by collecting the catalyst quickly, washing the catalyst with methanol, adding an internal standard, and determining gas chromatographically the amounts of organic compounds washed from the catalysts. These experiments gave highly irreproducible toluene contents, probably because of variable evaporation of the toluene under the conditions of isolation. Similar experiments performed at room temperature showed that the relative amounts of toluene and 1-bromooctane in the catalyst were the same as their relative amounts in the bulk organic liquid.[3]

Discussion

The aim of this research is to determine what experimental factors control the rates of reactions catalyzed by polymer-supported quaternary ammonium and phosphonium ions. Mass transfer of reactants to the particle surface, intraparticle diffusion, and intrinsic reactivity all are important under the most common triphase conditions.[3] The observed rates of reaction of cyanide ion and 1-bromooctane depend on the method of mixing of the triphase system. At 400–600 rpm under our conditions apparently optimum mixing is achieved, since the rates no longer show the stirring speed dependence observed at lower speeds. (With other equipment in other laboratories, the stirring speed required for optimum mixing might be quite different.) All experiments reported in this paper were performed with 400–440-rpm stirring, where mass transfer of reactants to the particle surface does not limit the observed reaction rates. Intraparticle diffusional limitations were revealed in the earlier work by decrease of the rates as catalyst particle size increased and as the degree of cross-linking of the polymer increased.[3] Intrinsic reactivity influence on the rates has been observed in many laboratories, in which different onium ion structures were shown to have different catalytic activities.[2]

The earlier results obtained with 2–10% cross-linked gel polystyrene supports did not establish whether the ion exchange (transport of cyanide ion from the particle surface to active sites) or transport of the organic reactant was the rate-limiting factor.[3] Transport of 1-bromooctane was assumed to be limiting because photographs of stirred reaction mixtures showed that the solid catalyst particles and the organic phase both were suspended in the continuous aqueous phase, suggesting better contact of the particles with the aqueous phase than with the organic phase.[3] Also, the cyanide ion was used in tenfold excess over 1-bromooctane to make the kinetics pseudo first order, dependent only on overall 1-bromooctane concentration. The observed kinetics typically showed gradual decreases in observed first-order rate constant in runs in which the final data point was taken after 25–80% conversion. Since a recovered catalyst had both reduced activity when it was recycled and a lower content of quaternary phosphonium ions, the decreases in rate constants with time were attributed to decomposition of the active sites during the kinetic runs. Only initial rate constants were used for comparison of particle size and cross-linking effects to minimize the influence of active-site decomposition on the results.

The data in Table III now reveal that the catalysts retain large amounts of the product bromide ion during kinetic experiments. Tundo[8] obtained similar results with silica gel supported catalysts in reactions of potassium bromide with *n*-octyl methanesulfonate. Our recovered catalysts also contained an average of 20% fewer ion exchange sites than the fresh catalysts. It would be informative to study the rates of both the ion exchange and active-site decomposition, but faster and more accurate analytical methods would be needed for such a study.

Conventional polystyrene-based ion exchange resins with benzyltrimethylammonium sites have selectivity factors $K_{\mathrm{Cl}}{}^{\mathrm{Br}}$ of about 3 for bromide ion over chloride ion in aqueous solutions.[9] The affinity of cyanide ion for the resin lies between that of bromide and that of chloride.[9] $K_{\mathrm{CN}}{}^{\mathrm{Br}} = 1.52$ for the 2% cross-linked and $K_{\mathrm{CN}}{}^{\mathrm{Br}} = 2.85$ for the 10% cross-linked macroporous catalysts were determined in this work. If the fractional attainment of ion exchange equilibrium can be determined as a function of time, ion diffusion coefficients inside the resin can be estimated from eq 4,

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \qquad (4)$$

in which $U(\tau)$ is the fractional attainment of ion exchange equilibrium, τ (dimensionless time) = $\bar{D}_{\mathrm{A}}t/r_0{}^2$, $\alpha = \bar{D}_{\mathrm{A}}/\bar{D}_{\mathrm{B}}$ is the ratio of diffusion coefficients of ions A and B, the f_i are functions of α, real time is t, and the particle radius is r_0.[10] Equation 4 has been solved numerically for many values of $U(\tau)$ and α. The selectivity factors and the ion contents of the recovered catalysts in Table III correspond with $U(\tau) = 0.65$ and 0.46 for the 2% and 10% cross-linked macroporous catalysts. The assumption of zero-order replacement of $\mathrm{Br^-}$ in the catalyst by $\mathrm{CN^-}$ in the presence of at least a 20-fold excess of $\mathrm{CN^-}$ in the external aqueous phase, the reaction times required to attain the percent conversion, and the ion contents of the 2% and 10% cross-linked macroporous catalysts in Table III permitted us to calculate times of 160 and 304 s that would be required to attain the ion contents in Table III in the absence of chemical reaction. If $\alpha = \bar{D}_{\mathrm{Br}}/\bar{D}_{\mathrm{CN}}$ lies in the range 0.5–2.0 for the phase-transfer catalysis experiments, the intraparticle diffusion coefficients of bromide and cyanide ion, $\bar{D}_{\mathrm{Br}}$ and $\bar{D}_{\mathrm{CN}}$, are $(0.6–1.0) \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ for the 2% cross-linked and $(0.12–0.20) \times 10^{-8}\ \mathrm{cm^-\ s^{-1}}$ for the 10% cross-linked macroporous catalysts. Values of $\bar{D}_{\mathrm{Br}}$ for ion exchange resins in aqueous suspensions are known for resins with different ionic groups and different degrees of cross-linking. Soldano and Boyd,[11] using nominally 8% divinylbenzene cross-linked resins at 25 °C, found that $\bar{D}_{\mathrm{Br}}$ in a benzyltri-*n*-butylammonium ion resin with a capacity of 0.96 mequiv/g (about the same as in our catalysts) was $5.5 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$. Their value of $\bar{D}_{\mathrm{Br}}$ at 25 °C is greater than the ones we estimate under phase-transfer catalysis conditions at 90 °C. The resin during phase-transfer catalysis is swollen mainly by toluene, since its swelling ratio is greater in toluene than in water.[3] Bromide and cyanide ions diffuse poorly through toluene. In a model for the interior of the catalyst,[12] the water is present only in hydration pools around the ionic sites, with the organic phase continuous throughout the polymer network. Ion transport may be slow because there is no continuous aqueous phase inside the particle.

With a 1% cross-linked polystyrene, 17% ring substituted with benzyltri-*n*-butylphosphonium ions, Ohtani and Regen[13] found that catalyst activity decreased greatly as the amount of water imbibed into the catalyst increased for reaction of chloride ion with *n*-decyl methanesulfonate in toluene with no external aqueous phase. A comparable triphase catalysis experiment showed higher activity than a biphase experiment with a fully hydrated catalyst because the osmotic effect of the external concentrated sodium chloride solution reduced the water content of the catalyst.[13] In triphase experiments the effect of ion concentrations in the aqueous phase is more complicated, and at least three factors need to be considered: (1) dependence of intrinsic reactivity at the active site on the degree of hydration of the catalyst (less hydration leads to higher activity), (2) dependence of ion exchange rate on the degree of hydration of the catalyst (the rate of ion exchange increases as the degree of hydration of the resin increases; this phenomenon is well-known in conventional ion exchange resins[9]), and (3) dependence of the ion exchange rate on the concentration of ions in the external solution (the ion flux is directly proportional to the concentration gradient between the surface of the particle and the interior of the particle; in a well-stirred solution the surface concentration is equal to the bulk concentration of ions in the external solution[14]). Careful experiments are needed on the effect of ionic strength on reaction rates in triphase catalysis. Decreasing concentration of the reactant anion in the aqueous phase might lead either to a faster rate, because increased hydration of the polymer leads to faster transport of ions to the active site, or to a slower rate, because increased hydration of the catalyst decreases its activity.

At the start of this investigation, we hoped to find higher catalytic activity with macroporous polystyrene supports. Rates of diffusion of reactants through the polymer matrix should be independent of macroporosity. However, a macroporous resin has greater surface area and shorter pathways from the surface to the active sites than a strictly microporous resin. One milliliter of cubes with edges 100 μm long has a surface area of 0.06 m^2/g, approximately equal to the total surface area of the nonmacroporous particles. The macroporous particles have additional surface area in the permanent pores, up to 588 m^2/g, as reported in Table II. The "macroporous" cataysts reported by Regen[5] had surface areas of <1 m^2/g, below the limit of detection of conventional nitrogen adsorption measurements.[6a]

The kinetic experiments with nonmacroporous catalysts shown in Figure 1 used 100/200-mesh (74–149 μm diameter) particles, with which the rates are known to be limited partly by intraparticle diffusion and partly by intrinsic reactivity at the active sites.[3] With a macroporous catalyst, transport of reactants to the active site could proceed both through the polymer matrix and through the liquid-filled permanent pores. Rates of diffusion through the pores should be the same as rates of diffusion through a quiet liquid and faster than through the cross-linked polymer network, according to previous studies of diffusion of ions and neutral molecules in ion exchange resins.[14] In spite of larger surface areas, the macroporous catalysts showed lower activity and only slightly less retention of bromide ion than the corresponding nonmacroporous catalysts. Ion transport through the macropores must be no faster than through the swollen polymer network, perhaps because the macropores are filled completely with the organic phase and not with water. The failure of water to penetrate the macropores might be attributed to the lipophilic character of the polystyrene surface. Greater catalytic activity might be expected of catalysts with more hydrophilic surfaces, although hydrophilic dextrans with quaternary ammonium active sites are highly active only when the surface is modified with lipophilic groups.[15] An appropriate hydrophile/lipophile balance is needed.

References and Notes

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Matrix Polymerization on Polyelectrolyte Backbones: Influence of Monovalent Salts on the Condensed Monomeric Counterions

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Received February 8, 1982

ABSTRACT: A detailed investigation of the system [2.2.2],4-ionene-pSSA in the presence of various counterions was undertaken. The affinity of counterions toward the polyelectrolyte was determined by ion-specific potentiometry and the polymerization kinetics of pSSA. A simple equilibrium between "condensed" and "atmospheric" counterions allowed expression of the affinity of the counterions in terms of a ratio of equilibrium constants $K_{\text{pSSA}^-}/K_{\text{C}^-}$, called the "affinity ratio". Good agreement between values of the affinity ratios determined by potentiometry and polymerization kinetics of pSSA was found. This confirms the applicability of the ion-condensation model of the polymerization process on ionene polyelectrolytes. The sequence of ionic selectivity found in water-rich media is $\text{ClO}_4^- > \text{I}^- > \text{Cl}^- > \text{F}^-$. This sequence was found to be strongly dependent on solvent composition (water–2-propanol). An inversion of the sequence is found in 2-propanol-rich media. The affinity changes explain the large influence of solvent composition on the polymerization kinetics of [2.2.2],4-ionene-pSSA. The variation of the affinity of the counterions is explained by their ionic hydration. For organic anions it was found that aromatic sulfonates have an affinity larger than that of aliphatic carboxylates. Here also, the trends can be explained by the differing hydration tendency of carboxylates and sulfonates.

Introduction

In a previous publication[1] the concept of counterion condensation was applied in order to interpret the polymerization kinetics of *p*-styrenesulfonate attached to a [2.2.2],4-ionene polycation matrix (obtained through condensation of 1,4-diazabicyclo[2.2.2]octane and 1,4-dibromobutane) such as given in Figure 1.

In the framework of this model the polymerization on the polyelectrolyte matrix should reflect the properties of the condensed monomeric counterions. The rate of polymerization is considered to be directly dependent on the fraction x of the condensed monomeric counterions. The value of x can be obtained for a given set of experimental conditions (pH, temperature, solvent, initiator concentration) from the dependence of the polymerization rate V_p of *p*-styrenesulfonate (pSSA^-) counterions on the $[\text{pSSA}^-]/[\text{ionene}]$ "filling ratio", r, for $r \leq 1$.

In the present work the relative affinities of various counterions toward the [2.2.2],4-ionene polyelectrolyte are determined by two independent methods. One of these involves the determination of the kinetics of pSSA^- counterion polymerization, and the other a potentiometric titration of free counterions by means of ion-specific electrodes.

Experimental (conductometric) data show that when r varies from 0 to 1, x varies from 0 to 0.68.[2] Kinetic data[3] indicate that matrix polymerization of ionene-pSSA complex is very sensitive to addition of NaCl, which produces a decrease in the polymerization rate. This effect has also been satisfactorily explained by counterions competing for condensation sites on the matrix.[1] Assuming a simple equilibrium of condensed and "atmospheric" counterions for the competing counterions C^- and pSSA^-, respectively,

$$\text{pSSA}^- + \text{ionene}^+ \rightleftharpoons \text{ionene-pSSA} \qquad (1)$$

$$\text{C}^- + \text{ionene}^+ \rightleftharpoons \text{ionene-C} \qquad (2)$$

From eq 1 and 2 one gets the following equilibrium constants:

$$K_{\text{pSSA}^-} = [\text{ionene-pSSA}]/[\text{ionene}^+][\text{pSSA}^-] \qquad (3)$$

$$K_{\text{C}^-} = [\text{ionene-C}]/[\text{ionene}^+][\text{C}^-] \qquad (4)$$

From eq 3 and 4 one obtains the "selectivity ratio":

$$\frac{K_{\text{pSSA}^-}}{K_{\text{C}^-}} = \frac{[\text{C}^-][\text{ionene-pSSA}]}{[\text{pSSA}^-][\text{ionene-C}]} \qquad (5)$$

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0024-9297/82/2215-1251$01.25/0