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Preparation of Sulfonated Resins as an Immobilized Phase-Transfer Catalyst for the Hydrolysis of Benzophenone Azine to Hydrazine[1,2]

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Sulfonated resins with a variety of acid-site distribution have been prepared and characterized to obtain highly active immobilized phase-transfer catalysts for conversion of benzophenone azine into hydrazine in a liquid–solid–liquid triphase system. Sulfonation of cross-linked polystyrene with concentrated H_2SO_4 under mild conditions gave various resins of lower acidity, but X-ray microanalysis revealed the acid-site distribution to be like an eggshell, showing that the spheres were sulfonated from the external surface toward a central core. Lipophilic resins with uniform acid-site distribution were obtained by the ternary copolymerization of sodium *p*-styrenesulfonate, styrene, and divinylbenzene in aqueous dimethylformamide. The acidity of resins could be predicted based on the monomer content in the charge. The competing imbibition of two insoluble liquids, toluene and water, by sulfonated resins balanced at 0.8 meq/g, in good agreement with the optimum acidity for azine conversion. The value corresponds to a sulfonic group per five pendant phenyl groups of the skeletal polymer. Effect of particle size of ternary gel catalyst on the rate of azine conversion suggested the predominant contribution of acidic sites on the surface. Attempts were made to expose available sites on the surface as much as possible employing porous texture under the balanced-wetting environment. Thus moderately sulfonated resins with a macroreticular structure showed high activity for azine conversion. A reactor device capable of continuous operation of liquid–solid–liquid triphase catalysis in a flow system and the results of an illustrative run with 90% conversion over 50 h on-stream are also described.

INTRODUCTION

A cyclic catalytic process for hydrazine synthesis from benzophenone, ammonia, and molecular oxygen via the azine with recycling of benzophenone has been proposed by the authors (*1–3*).

$$Ph_2C{=}O + \boxed{NH_3} \rightarrow Ph_2C{=}NH + H_2O \qquad (1)$$

$$2Ph_2C{=}NH + \tfrac{1}{2}O_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2 + H_2O \qquad (2)$$

$$Ph_2C{=}N{-}N{=}CPh_2 + 2H_2O \rightarrow 2Ph_2C{=}O + \boxed{N_2H_4} \qquad (3)$$

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[1] Ammonia-Hydrazine Conversion Processes. XVII. The previous paper (Part XVI) is Ref. (*4*).

[2] Caution: Hydrazine should be handled with care. It is a *poisonous* liquid and *explodes* during distillation if traces of air are present. Toxicity of hydrazine is summarized in Ref. (*11*), covering hazard index; metabolic action; therapy and prophylaxis; acute and inhalation toxicity; nervous, skin, eye, carcinogen, and mutagenic effects.

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The process involves acid-catalyzed hydrolysis of azine into hydrazine (Stage 3), for which lipophilic sulfonic acids revealed excellent activity under phase-transfer conditions (*4*). Thus an attempted hydrolysis of azine in a two-phase system of xylene and dilute aqueous sulfuric acid gave unfavorable results of 0.9% conversion of azine with 0.6% yield of hydrazine at 100°C for 1 h, while in the presence of lipophilic sulfonic acids such as dodecylbenzenesulfonic acid, hydrazine was obtained dramatically in high yields (89.9–93.2%) under similar conditions (*4*).

To simplify the catalyst separation, attempts were extended in the present work to apply sulfonated results as an immobilized phase-transfer catalyst. Commercially available resins were highly sulfonated and much too hydrophilic for the present purpose. Sulfonated resins with a variety of acid-site distributions were prepared and characterized, leading to a conclusion that the well-balanced wetting of an acidic solid both with organic and aqueous phase would be essential for a highly active immobilized phase-transfer catalyst. A reactor device capable of continuous operation of liquid–solid–liquid triphase catalysis in a flow system and the results of an illustrative run with 90% conversion over 50 h on-stream are also described.

EXPERIMENTAL

Apparatus and procedure. Activity of various sulfonated resins for conversion of benzophenone azine into hydrazine was compared at a standard condition given below. A round-bottom flask fitted with a reflux condenser was charged with 25 cm^3 of xylene and 3.6 g (10 mmol) of benzophenone azine at 90°C. To the clear solution was added 25 cm^3 of 2 *N* H_2SO_4 and 1.0 g of a sulfonated resin (100–200#) as catalyst. The solution was stirred magnetically (Magmixer MD-81, Yamato, Tokyo) at 500 rpm, which was calibrated with a tachometer (Model 3632 of Yokogawa–Hokushin, Tokyo). After 1 h of reaction at 90°C, the catalyst was filtered and then analyzed similarly as described in the previous paper (*4*). A continuous flow operation for triphase catalysis was also made. The reactor descriptions are given in the text.

Characterization of catalysts. An aliquot of a dried resin (~1 g, 60 - 100#) was wetted with a small amount of ethanol, soaked overnight in 20 cm^3 of $\frac{1}{4}$ *N* NaOH, filtered, washed with water, and titrated for the residual alkali with $\frac{1}{10}$ *N* HCl to determine the total acidity of the resin. Acid-site distribution of sulfonated resins was examined by EPMA (Model JXA-50A, JOEL, Tokyo) for sulfur. The texture of polymer catalysts was observed by SEM (Type α-9, Hitachi–Akashi, Tokyo). Samples were covered by a sputtered film of Au–Pd alloy (Ion Coater IB-5, Eiko-Eng., Naka, Ibaraki). Skeletal density of catalyst was measured by a Wadon pycnometer employing toluene as soaking liquid. Surface area was determined by a conventional nitrogen adsorption method (Shibata P-700, BET apparatus). Amounts of two insoluble liquids imbibed by a sulfonated resin were determined as a measure of hydrophilic and/or lipophilic nature. To a two-phase system of 25 cm^3 of both toluene and water was added 1 g of a dried resin (100–200#) and stirred vigorously. After removal of liquids in the interparticle void space by filtration, two liquids were eluted with ethanol and analyzed by gas chromatography (10% PEG 4000/Flusin T; 3 mm$^{\phi}$ × 2 m; Hitachi 163-TCD).

Materials. Benzophenone azine was prepared and purified as described in the previous paper (4). Sodium *p*-styrenesulfonate was purchased from Tokyo Kasei Co., and used as received. Monomers of styrene (61–73°C/40- to 55-mm Hg) and divinylbenzene (56–63°C/4- to 5-mm Hg) were distilled under nitrogen prior to polymerization. Modified Amberlite resins were provided by Organo Co. Ltd, Tokyo. These resins have porous texture the same as that of Amberlite 200 C(4.69 meq/g), but have different acidity: NH-914, 0.46 meq/g; NH-909, 1.50 meq/g; NH-910, 2.52 meq/g.

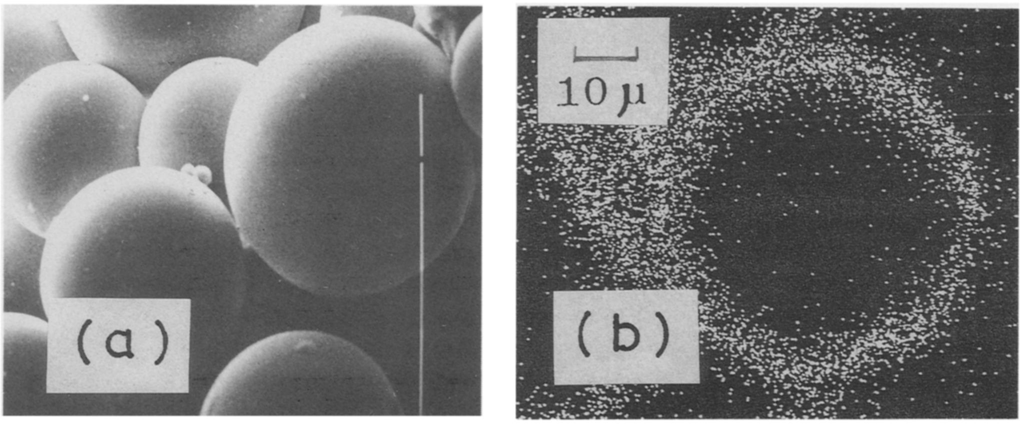

FIG. 1. Scanning electron microscopic texture of skeletal copolymer (a) and acid-site distribution of the sulfonated resin (b).

RESULTS AND DISCUSSION

A schematic view of immobilized phase-transfer catalysis by sulfonated resins for conversion of benzophenone azine into hydrazine might be summarized as follows[3]. When an organic droplet was in contact with the hydrated acidic site ($-SO_3H \cdot nH_2O$) on the catalyst surface, hydrolysis of azine occurred to afford benzophenone and hydrazine. On removal of the organic droplet from the surface, hydrazine trapped on the acidic site ($-SO_3N_2H_5$) was washed out in the aqueous phase to regenerate the effective acidic site. Thus the preparation strategy of highly active immobilized phase-transfer catalyst should be based on the well-balanced imbibition and wetting of an acidic solid both with the organic and the aqueous phase.

Preparation of Sulfonated Resins with Various Acid-Site Distribution

Sulfonated resins such as Amerlite IR-120 B, 200 C, Amberlyst 15, and Dowex 88 are available commercially. However, these resins are highly sulfonated, with acidity of 4.3–4.7 meq/g, and were much too hydrophilic for the present purpose. No reaction was observed for Amberlite resins suspended in a two-phase reaction mixture of toluene containing azine and aqueous sulfuric acid.

Acid-site distribution like eggshell. Suspension copolymerization of styrene and divinylbenzene under the following conditions (*5*) gave spherical cross-linked polystyrene with 20–50 μm in diameter, as shown in Fig. 1(a): 15% DVB (v/v), AIBN 0.4% (wt/v-org.), monomer dilution ratio (monomer/total org.) $F_M = \frac{1}{4}$ (v/v), org./$H_2O = \frac{1}{2}$ (v/v), 90°C, 20 h under nitrogen. The resultant copolymer reversibly swells in toluene up to the reciprocal monomer dilution ratio ($1/F_M = 4$), signifying the expanded gel structure.

Suspending 3 g of copolymer in 15 cm^3 of concentrated H_2SO_4 ($d = 1.84$) afforded sulfonated resins with various acidity as shown in Fig. 2. Inspection by EPMA for sulfur revealed that the intraparticle acid-

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[3] A referee suggested another view, which may be a more likely portrayal. The hydrophilic–hydrophobic balance of the catalyst may allow both wetting of the catalyst by the continuous liquid phase and close contact by droplet adsorption, thereby allowing close proximity to the catalyst sites of the dispersed reactant. This situation would allow easy diffusive replenishment of the dispersed phase reactant at the active site, due to a very short diffusive path.

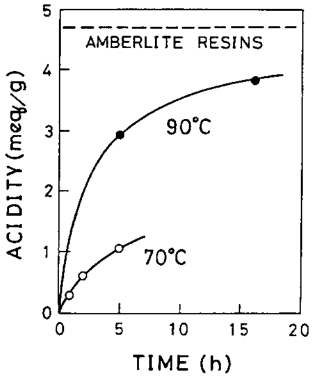

FIG. 2. Sulfonation of cross-linked polystyrene with conc. H_2SO_4. Skeletal polymer: 15% DVB, expanded gel; H_2SO_4/polymer = 9.2 (w/w).

site distribution was not uniform but the eggshell type, as shown in Fig. 1(b), showing that the spheres were sulfonated from external surface toward central core.

Uniform acid-site distribution. Another approach to prepare sulfonated resins with uniform acid-site distribution was made, employing *p*-styrenesulfonate as a starting monomer. The conventional suspension polymerization procedure was unfavorable for the present ternary system due to the hydrophilic nature of *p*-styrenesulfonate. Wiley and Reed (*6*) obtained ternary copolymers of potassium *p*-styrenesulfonate, styrene, and divinylbenzene in high yields of 91–94% in dimethylformamide (DMF) as solvent. However, precipitation was observed (*6*) in the initial stage of polymerization, as early as after 10 min, suggesting the yield of the mechanical mixture of powder with different acidity. Accounting for the hydrophilic nature of sulfonate, an appropriate amount of water was added in DMF to avoid precipitation.

Thus ca. 10 g of a monomer mixture in a given ratio was dissolved in 50 cm^3 of DMF/H_2O = 4/1 (v/v) containing 0.4% (wt/v) AIBN and stirred at 80°C under nitrogen. The clear reaction liquor clouded gradually without precipitation to form swollen gel. A translucent swollen gel, for 15% DVB, and an opaque white mass wetted with solvent, for 40% DVB, were obtained after 20 h. The resultant copolymer was washed with an excess of acetone, converted $-SO_3Na$ to $-SO_3H$ with 1 *N* HCl, washed with water, and then dried overnight at 80°C.

Figure 3 shows the uniform acid-site distribution of these ternary copolymers. The flat and featureless texture of a shrunken gel, for 15% DVB, and macroreticular porous aggregate, for 40% DVB, were observed by SEM, as shown in Fig. 4.

These results provide a general procedure for preparation of sulfonated resins with various textures, with lower acidity, and with uniform acid-site distribution. Polymer acidity could be predicted as shown in Fig. 5, adopting an appropriate composition of monomers in the charge.

Properties and Activity of Catalysts

Wetting and activity. Imbibition of a liquid by a porous solid is a phenomenon highly

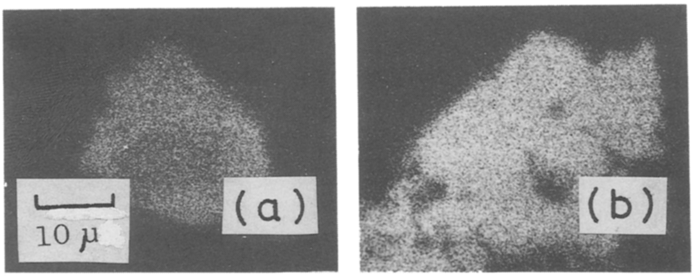

FIG. 3. Uniform acid-site distribution of ternary gels. (a) EG-3, 0.89 meq/g, (b) EG-4, 2.32 meq/g.

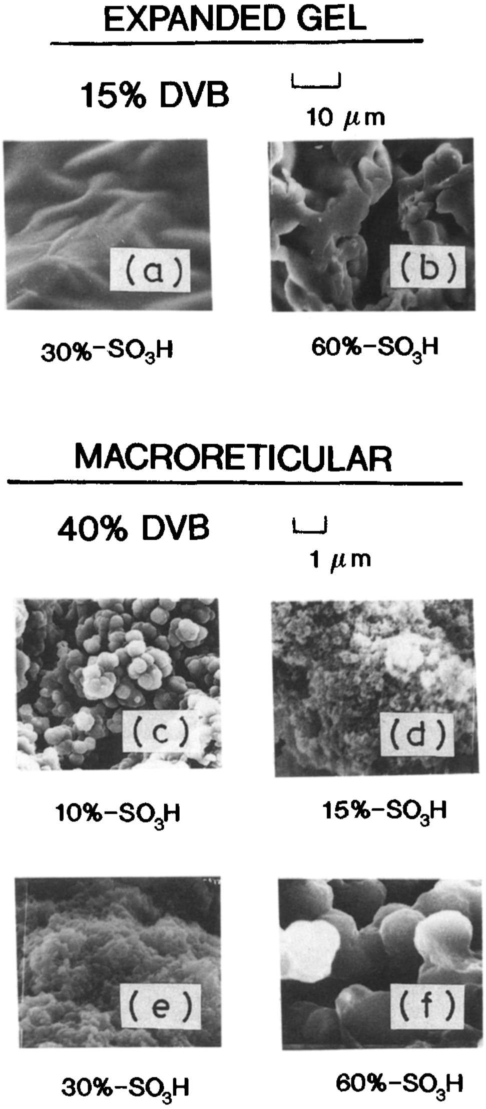

FIG. 4. Scanning electron microscopic texture of ternary copolymers.

dependent on wetting (*7*). Critical surface tension of γ_c = 33 dyn/cm of polystyrene (*8*) is a medium value of the liquid surface tension of water (72.7) dyn/cm) and toluene (28.4 dyn/cm). Thus toluene wets water-repelling polystyrene. Immersion of polystyrene in sulfuric acid resulted in a drastic decrease in contact angle for water (*9*), presumably due to formation of surface sulfonic groups.

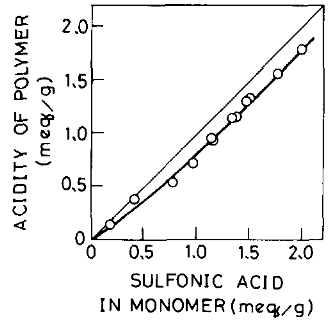

FIG. 5. Prediction of polymer acidity based on the acid content in polymerization at H_2O/DMF = 15/85 (v/v).

Figure 6 compares the imbibition behavior of two insoluble liquids (toluene and water) by sulfonated resins, and the activity of resins as an immobilized phase-transfer catalyst for conversion of benzophenone azine into hydrazine. High values of toluene uptake were observed for lipophilic resins with lower acidity. Water uptake increased in place of a decrease in toluene uptake with increasing acidity. The rigid structure of macroreticular resins (a) leads to saturation

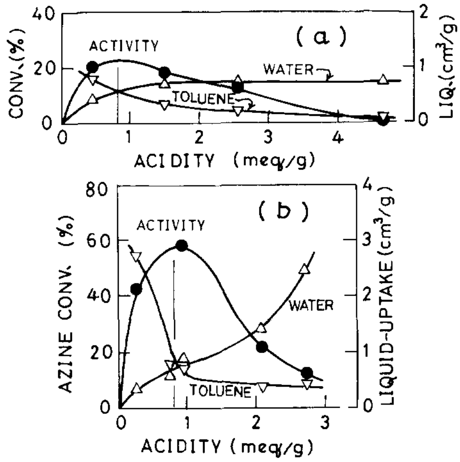

FIG. 6. Activity of sulfonated resins as immobilized phase-transfer catalyst for conversion of benzophenone azine into hydrazine (●), and imbibition of water (△) and toluene (▽) by the resins. (a) Modified Amberlite, (b) ternary gel with uniform acid-site distribution. Conditions: 90°C, 1 h, 500 rpm, catalyst 1 g.

behavior for water uptake, while expanded gel (b) capable for swelling allowed higher water uptake at a higher acidity region. It is of interest that the uptake balanced with that of water at 0.8 meq/g for both series of resins (Fig. 6 (a) and 6(b)). The value of acidity of 0.8 meq/g corresponds to a sulfonic group per five pendant phenyl groups of the skeletal polymer.

It seemed likely that sulfonated resins with lower acidity might show affinity for the organic phase. Modified Amberlite resins (a) with lower acidity converted azine, while no reaction was observed for highly acidic Amerlite 200 C. Ternary gels with uniform acid-site distribution (b) showed higher activity. For both series of catalyst, the activity was strongly dependent on acidity. Maximum conversion was observed at 0.8 meq/g, a value quite close to the acidity of balanced wetting of the resins with insoluble two liquids, toluene, and water, in the triphase system.

Stirring rate. No differences in conversion were observed for 200 and 500 rpm. The stirring rate of 200 rpm is in the lowest agitation level to disperse liquid droplets. Thus the balanced wetting of the acidic sites with two insoluble liquids, rather than liquid–liquid dispersion, would be a predominant factor for high activity in triphase system.

Acid-site density. Catalysts prepared by sulfonation of polystyrene showed a somewhat different activity pattern. No effect of acidity on the azine conversion was observed for a series of expanded gels of eggshell type acid-site distribution, as shown in Fig. 7, in sharp contrast with the catalysts from ternary copolymers (Fig. 6). The acidity of catalysts given in Fig. 7 covers a wide range of 0.25_5–3.8_2 meq/g, but the acid-site density on the external surface would be similar together. The acidic sites of these catalysts are accumulated near the surface as evidenced in Fig. 1(b). In the case of catalysts with uniform acid-site distribution (Fig. 3), total acidity would be an adequate measure for the acid-site density.

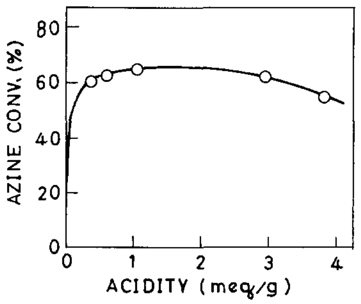

FIG. 7. Effect of acidity of expanded gels with acid-site distribution like eggshell on the azine conversion. Conditions: same as in Fig. 6.

Particle size and effective sites available. Figure 8 (a) illustrates apparent first-order kinetics in the present triphase catalysis for conversion of benzophenone azine into hydrazine. The rate constant (k) increased with increasing the reciprocol particle radius ($1/r_0$) for an active ternary gel of optimum acidity with uniform acid-site distribution as shown in Fig. 8 (b).

The external surface area per unit weight of catalyst is inversely proportional to the particle radius as

$$S = (4\pi r_0^2 n) / (4\pi r_0^3 \rho n/3) = 3/\rho r_0,$$

showing the predominant contribution of sites on the surface. Thus grinding of gel

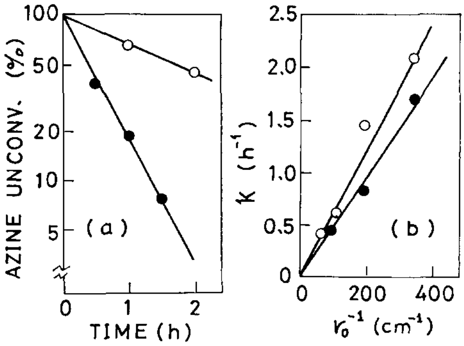

FIG. 8. Apparent first-order kinetics (a) and effect of particle radius on the rate constant (b). Conditions: 90°C, 1 g, 500 rpm, (○) EG-31 (1.16 meq/g), 42–60 # for (a) (●) EG-3 (0.89 meq/g), 200–300 # for (a).

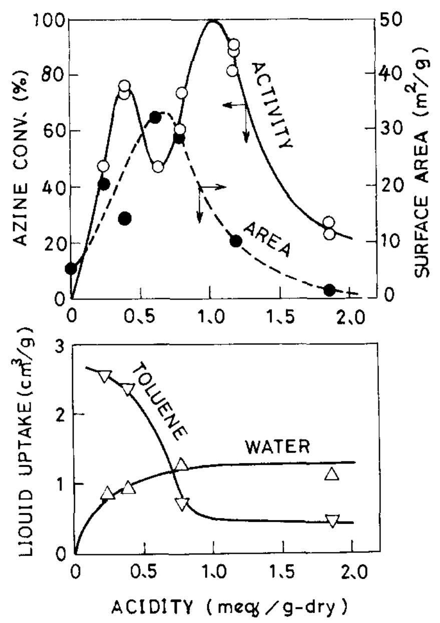

FIG. 9. Activity, surface area, and liquid-imbibition behavior of macroreticular ternary copolymers. Conditions: same as in Fig. 6.

particles increases external surface in favor of exposing the effective sites. However, the reaction was conducted in the triphase system, where the solid particle should contact with two liquids, and fine particles less than droplets in size might cause reduction of the liquid–solid–liquid contact efficiency arising from longer floating in one of the two liquids. The droplet size in the present system was estimated as ~100 μm and the minimum size for gel catalysts would be 200–300 # in practice.

Active catalysts with macroreticular porous texture. Another approach to exposure of acidic sites on the surface is the utilization of porous texture, which leads to high surface area even for a large particle. Highly active catalysts showing the azine conversion over 90% at 90°C for 1h could be obtained as shown in Fig. 9.

The balanced wetting of the acidic sites with two liquids, as presented in Fig. 6, was again a parameter affecting the catalyst activity, also for porous resins. However, the activity pattern for porous resins dropped at 0.6 meq/g, where the surface area of catalyst showed a maximum as high as 32.4 m^2/g. Droplets of two mutually insoluble liquids should move in shifts through pore space.[3] It seems reasonable that capillarity causes insufficient transfer of liquid through narrow pores less than 0.1 μm.

Continuous Flow Operation in Triphase Catalysis

A mixer settler equipped with a baffled agitater followed by a separation zone is a common reactor for two immiscible liquids (*10*). An additional problem in the continuous operation of a triphase system is how to prevent the loss of catalyst particles. Fixed-bed operation is unfavorable for the present purpose due to insufficient contact among the liquid–solid–liquid system.

The reactor device given in Fig. 10 has been proposed by the authors in the present work. Light liquid (azine/xylene) and heavy liquid (2 *N* H_2SO_4) were introduced countercurrently to a tower reactor. Catalyst powder mounted near the liquid–liquid interface was agitated vigorously to promote triphase contact. The skeletal density of polymer catalyst should be in a medium value between the densities of two liquids as shown in Fig. 11. Catalyst particles that are forced up into the light liquid then sediment spontaneously, and those forced down into the heavy liquid refloat up to the agitated zone.

Figure 12 illustrates the results of conversion of benzophenone azine into hydrazine in a continuous-flow operation with 90% conversion during over 50 h on-stream. It should be emphasized that no reaction was observed for highly sulfonated Amberlite resins. The excellent results given in Fig. 12 are the cumulative consequnce of an optimum acidity for the balanced wetting of acidic sites with two insoluble liquids, porous texture in favor of exposing effective sites on the surface, and a reactor device capable of continuous operation in a flow system without physical loss of the catalyst particles.

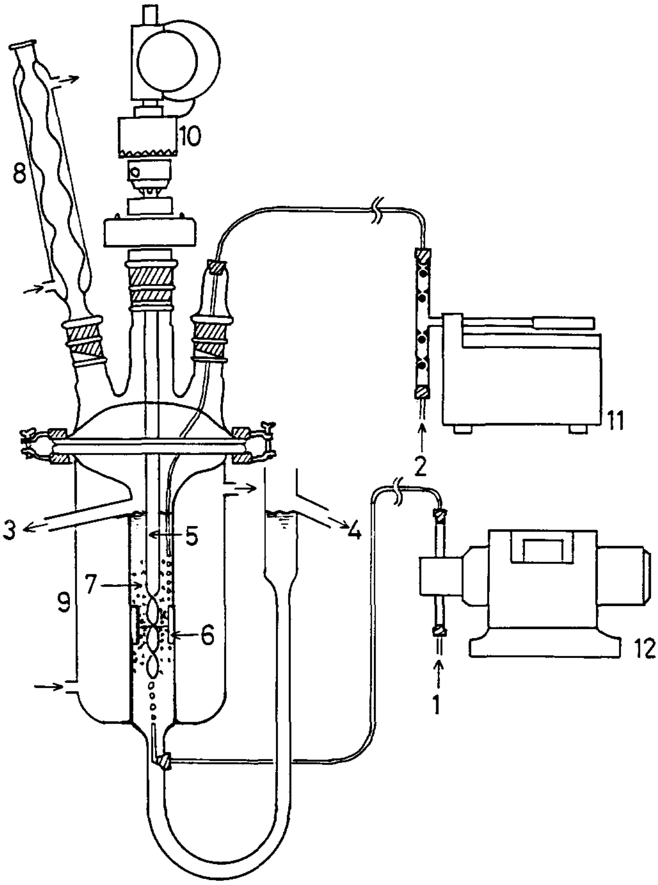

FIG. 10. Apparatus for continuous-flow operation in triphase catalysis. (1, 3) Light liquid (azine/xylene) inlet/outlet, (2, 4) heavy liquid (2 N H_2SO_4) inlet/outlet, (5) stirrer, (6) baffle, (7) catalyst, (8) reflux condensor, (9) heating oil jacket, (10) motor, (11, 12) plunger pumps.

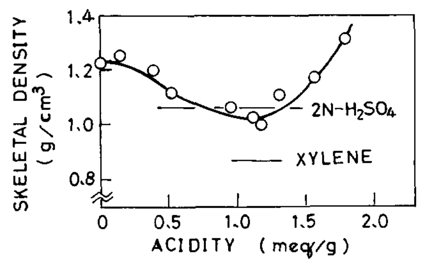

FIG. 11. Skeletal density of sulfonated resins (ternary copolymers) with macroreticular porous texture.

CONCLUSION

Moderately sulfonated resins with macroreticular porous texture revealed excellent activity as an immobilized phase-transfer catalyst for the hydrolysis of benzophenone azine to hydrazine. The well-balanced wetting of the acidic sites on the catalyst surface with two insoluble liquids, rather than liquid–liquid dispersion, would be a predominant factor for high activity in triphase catalysis. A reactor device capable of continuous operation in a flow system without loss of the catalyst particles was proposed with the results of an illustrative run.

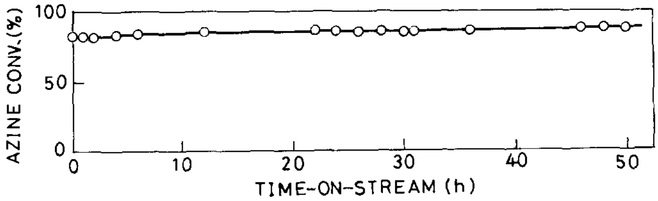

FIG. 12. An illustrative run for conversion of benzophenone azine into hydrazine by immobilized phase-transfer catalysis in a continuous flow operation. Catalyst: MR-46 (1.12 meq/g, 60–100 #, 2.0g); $[\text{Azine}]_0$ = 40 mmol/liter, θ_{org} = 1.0 h; 90°C; 600 rpm.

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