

Synthesis and Spectral Characterization of Surface-Enriched Polymer-Supported Phase Transfer Catalysts and Their Effects on Alkylation of Phenylacetone

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ABSTRACT: Polymer-supported phase transfer catalysts with active sites mostly on the surface were prepared by suspension copolymerization of styrene (St), divinylbenzene (DVB), and vinylbenzyl chloride (VBC) with AIBN, followed by the quaternization of the resulting copolymer beads with triethylamine. Active sites on the surface were achieved by the delayed addition of functional monomer (VBC) to the partially copolymerized St/DVB. Polymer beads enriched with active sites were characterized by SEM, EDAX, FTIR, and ESCA. The electron micrographs showed that the exterior surface of delayed-addition functional monomer catalysts (type 1) has a large number of nodules attached to the surface compared to the smooth surface exhibited by the conventional type 2 catalyst upon the simultaneous addition of all three monomers. In the EDAX analysis up to a depth of 100 Å, the surface chloride of type 1 peak intensity is greater (compared with type 2), indicating the $-\text{CH}_2\text{Cl}$ enrichment on the surface. In FTIR, the peak intensities of the C—N stretching (quaternary onium group) in type 1 are greater than those of type 2, confirming the evidence of more quaternization on the surface than in the bulk. From ESCA analysis to a depth of about 30 Å, it was found that type 1 (beads) contains 26% and type 2 contains 14% of covalent chloride on the surface, which strongly supports the grafting of VBC on St/DVB. In the estimation found by the Volhard method, type 1 has 4.73 meq g^{-1} and type 2 has 2.29 meq g^{-1} of ionic chloride, thus supporting the surface grafting of VBC. The catalytic activity of these two different catalysts was tested by studying the reaction, that is, the C-alkylation of phenylacetone. The rate constants of this reaction for type 1 are almost twofold greater than those of type 2, a finding that could uphold the preceding experimental observations. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 408–418, 2000

Key words: surface-enriched; active site; polymer-supported phase transfer catalyst; partial polymerization time; semiquantitative

INTRODUCTION

The polymer-supported phase transfer catalysts (PSPTC) frequently have been employed in or-

ganic synthesis because of their advantages of efficacy, easy separation, and reuse.^{1–8} The performance of supported catalyst is strongly dependent on the physical and chemical nature of immobilized materials^{9,10} and a great deal of attention has been focused on the development of various effective catalyst support due to their drastic enhancement in catalytic activity.^{11,12} Regen, who was the first to introduce “triphase catalyst,” has pointed out that the polymer is the most suitable support for immobilizing the phase

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transfer catalysts.^{13,14} Surface morphology and chemical nature are very important in the surface reactions because many chemical reactions take place on the particle surface.¹⁵ When conventional methods¹⁶ are employed to prepare polymer-supported bead-shaped catalysts, the slow diffusion of organic substrates into and out of the polymer matrix often limits their utility.^{17,18} To alleviate this difficulty, we have made an attempt to synthesize bead-shaped catalysts possessing active sites mostly on the surface.

Further, although there are numerous studies on the surfaces of inorganic catalysts, the study of surface characterization of polymer-supported catalysts is in the infant stage.¹⁹ Reilley et al.²⁰ investigated the polymer-anchored metal complexes. Tang et al.²¹ applied ESCA to characterize commercialized ion-exchange resins. Recently, Ruckenstein et al.²² calculated the surface composition of bound benzyl chloride groups of the polymer particles obtained by emulsion polymerization, by means of energy-dispersive X-ray analysis (EDAX). Hong et al.¹⁸ studied the surface morphology by SEM and also determined the onium and chloride ions on the surface of the polymer particles through electron spectroscopy for chemical analysis (ESCA).

In this work, we report a modified procedure for the preparation of copolymer beads containing VBC (active-site functional monomer) grafted onto the surface, their characterization by microscopic and spectroscopic techniques, and their catalytic activity on C-alkylation of phenylacetone with 1-bromobutane.

EXPERIMENTAL

Materials

Styrene (Fluka), divinylbenzene (Fluka), and vinylbenzyl chloride (p/m isomeric mixture, Dow-USA) were used as received without the removal of inhibitors. A polyvinyl alcohol (Fluka) and gelatin (AR, BDH) combination was used as the suspension stabilizer. Boric acid, triethylamine, acetonitrile, and methanol (S.D. fine, AR) were used as such without further purification. AIBN (Kochlight, USA) was recrystallized from ethanol. Phenylacetone (Fluka), 1-bromobutane (BDH), and sodium hydroxide (Merck) were used as such in the reaction.

Synthesis of Crosslinked Polystyrene Beads Enriched with Vinylbenzyl Chloride on the Surface by Suspension Polymerization Method

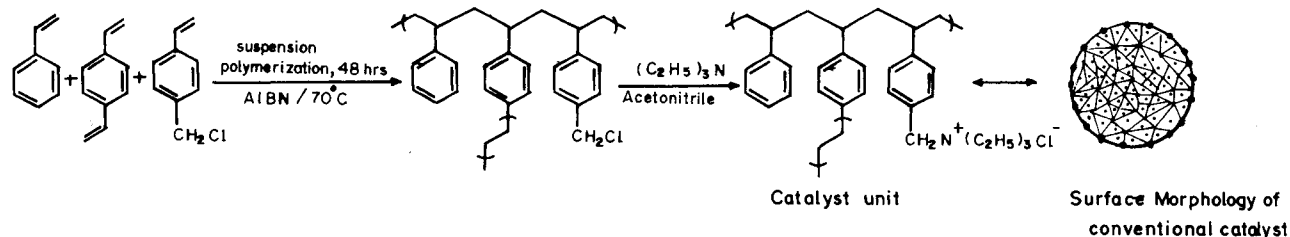
The typical procedure for the preparation is as follows: by fixing 6% crosslinking (DVB) and 25% active site (VBC), the organic phase was maintained at 82.5 g and aqueous phase at 225 g. Exactly 1.35 g of gelatin, 2.55 g boric acid, and 2.25 g of polyvinyl alcohol were thoroughly dissolved in 35, 60, and 130 ml of double-distilled hot water (50°C), respectively. These solutions were then mixed together at room temperature. The pH of the mixed solution was increased to 10 with 25% aqueous sodium hydroxide solution and 0.1 g of sodium nitrite. It was then transferred to a 500-ml three-necked RB flask equipped with mechanical stirrer (Remi Motor, OH) and reflux condenser. Nitrogen was passed continuously and the temperature was fixed at 50°C. After 0.5 h (maintaining the previous condition), the organic phase containing 9.90 g divinylbenzene, 51.98 g styrene, and 0.4125 g AIBN was thoroughly mixed and added to the reaction flask. Subsequently, the thermostat temperature was increased to 70°C and the stirring speed was maintained at 400 rpm using a tachometer (Teclock, Japan). The polymerization of styrene and divinylbenzene was allowed to proceed up to 12 h [partial polymerization time (PPT)] and then 20.66 g of VBC was added drop by drop to the reaction flask via addition funnel. The duration of addition was maintained to 1 h and the polymerization (Scheme 1) was allowed to go to completion (48 h, which includes PPT).

The polymer beads (type 1) obtained were washed with hot water and methanol until the wash solution did not turn cloudy upon the addition of water. Similarly, conventional¹⁶ type of copolymer beads (type 2) was prepared where the functional monomer VBC was added simultaneously along with St/DVB without allowing PPT. The conditions and quantities of aqueous and organic phase were maintained identically as in the earlier procedure. The polymer beads of both processes were dried at 60°C in a vacuum oven for 2 days and were later carefully sieved to obtain different mesh sizes using RO-TAP testing sieve shaker (W.S. Tyler Co., Cleveland, OH).

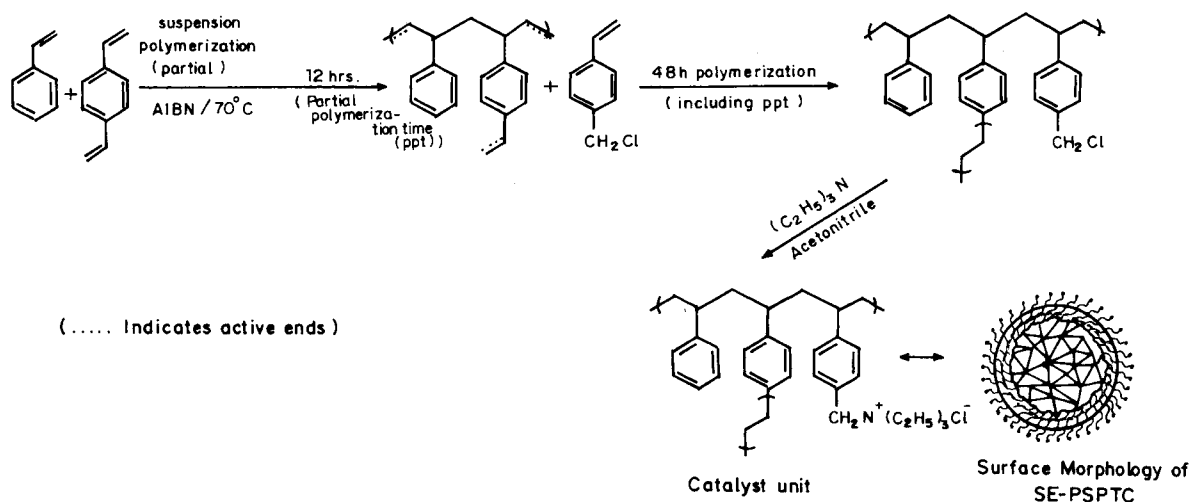
Preparation of Surface-Enriched Polymer-Supported Phase Transfer Catalyst (SE-PSPTC)

The surface-enriched (with active sites) polymer-supported phase transfer catalyst (SE-PSPTC) used

A. Preparation of conventional PSPTC using vinylbenzyl chloride as a functionality (Type-2)



B. Preparation of surface-enriched PSPTC (modified method): (Type-1)



Scheme 1

in this study was prepared by the addition reaction of the reactive type 1 copolymer beads with triethylamine (TEA).³ Five grams of (170–200 mesh size) type 1 beads and 150 ml of acetonitrile with 25 ml triethylamine were transferred to a 250-ml two-necked RB flask. The mixture was purged with nitrogen, deaerated under vacuum, and the whole setup was placed in an oil bath. The mixture was refluxed at 70°C for 3 days with continuous sweep of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with acetonitrile and methanol and dried under vacuum at 60°C. The dried beads were the surface-enriched PSPTC type. Similarly, type 2 copolymer beads were also converted into catalysts by adopting the above-mentioned procedure. The chloride ion concentration was estimated as per the procedure in literature.^{23,24}

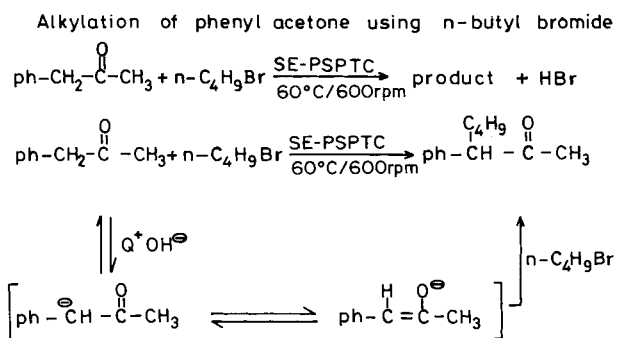
Preparation of Specimen for Surface Characterization Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Analysis (EDAX)

Equal quantities of 170–200 mesh size surface-enriched beads of type 1 and conventional beads

of type 2 were carefully fixed on the surface of a circle-shaped copper disk pivoted individually by rod. The beads spread on the surface of the copper disk were subjected to identical gold coating to eliminate the nonconducting behavior. These specimens were analyzed with 501-Philips scanning electron microscope interfaced with energy-dispersive X-ray analysis (EDAX). In applying this EDAX analysis as a semiquantitative measurement, care was taken to ensure identical gold coating. The operating signal was maintained at 25 keV and detection depth was about 100 Å. Due to identical gold coating, the gold deposited on the surface of both catalysts was constant and the peak area of Au was constant; only the peak area of Cl may be varied. For comparative purposes, the amounts of Au and Cl were accounted through an in-built module of the instrument and it executed the normalized EDAX spectrum based on the Au amount of the sample.

FTIR

Infrared absorption spectra of SE-PSPTC and type 2 catalyst were recorded with a Nicolet



Scheme 2

20DXB FTIR Spectrophotometer using the KBr grate. The ratio of sample and KBr was maintained constant in both catalysts while making the pellets. Since we are using this technique as a semiquantitative study, adequate care was taken to prepare the pellets. The characteristic peak (C—N, C—Cl) intensities were measured by the baseline method technique.²⁵ Absorbance [$\log(I_0/I)$] of the peaks was calculated from the height of the radiation energy (I_0) and height of its transmittance (I), which in turn gave the concentration of the respective peaks.

Electron Spectroscopy for Chemical Analysis (ESCA; XPS)

The VG ESCA MK200X was used for XPS analysis. The base pressure of the analysis chamber was 8×10^{-10} mbar. Al K X-ray (1486.6 eV) was used as the exciting source and pass energies of 100 and 20 eV were used for data collection. The system binding energy was standardized by AU 4 $f_{7/2}$ line, which was observed at 83.3 eV. Both samples were put onto indium foil, pressed, and then baked for 1 h at 60°C, before being loaded into the analysis chamber. All the data-collecting parameters were kept the same for both samples and the depth of information limit was about 30 Å. The instrument resolution was 0.8 eV. The percentage of surface chlorine and carbon were calculated using suitable software (Eclipse).

Efficiency of Catalysts in the Alkylation of Phenylacetone

Alkylation of phenylacetone with 1-bromobutane (Scheme 2) was carried out under pseudo-first-order conditions using both catalysts (type 1 and type 2) to examine the reactivity. In a 150-ml three-necked flask fitted with a 40×18 -mm stirrer, a curved Teflon blade was immersed in a water bath. Then the flask was charged with 25

ml of 1-bromobutane, 0.2 g catalyst, 45 ml sodium hydroxide (45% W/W), and hexadecane (1 ml internal standard) and stirred at 100 rpm for 10 min to condition the catalyst at 60°C. Phenylacetone (2 ml maintained at 60°C) was added and the stirring speed was increased to 600 rpm. The reaction was carried out up to 35 min. At definite intervals (5 min), samples were withdrawn from the organic phase of the reaction mixture and were quantitatively analyzed by gas chromatograph (Varian-3700 interfaced with Vista CDS 401 systems) with flame ionization detector. The column used for the product analysis was 10% SE-30, chrom WHP 80/120, 3 m \times 1/8 diameter stainless tube. The reaction rates were computed by following the disappearance of phenylacetone. The recycled and regenerated catalysts (both types) were also employed, using the same reaction with the view to know the reaction efficiency compared to the original. The pseudo-first-order rate constants were evaluated from the plots of $\log(a - x)$ versus time and the rate constant values are presented in Table I.

RESULTS AND DISCUSSION

Although there were a number of studies on the preparation of microporous bead-shaped insoluble polymer-supported catalysts in literature, there is no report on the study of surface-enriched (with active sites mostly on the surface) polymer-supported catalyst by suspension polymerization. Further, right from the initial period of PSPTC, because of reactive chloromethyl group in VBC, it has traditionally been used as a precursor for functionalization. Since VBC is a costly monomer, any researcher would appreciate not wasting the functional groups embedded inside the beads. Whenever conventional (type 2) preparation of crosslinked polystyrene beads was involved, the

Table I Activity of Catalysts in the Reaction of Alkylation of Phenylacetone

Reaction Stage	Type 2 Catalyst $k_{\text{obs}} \times 10^4, \text{s}^{-1}$	Type 1 Catalyst $k_{\text{obs}} \times 10^4, \text{s}^{-1}$
Original catalyst	1.96	4.10
Recovered (first time)	1.34	3.88
Recovered (second time)	1.06	3.75
Regenerated	1.58	4.02

simultaneous addition of functional monomer to the supporting monomers, St/DVB, led to the possibility of this expensive monomer's being buried inside the polymer network. Further, when it was made into catalyst by reacting with tertiary amine, it was not possible to convert all the pendant benzylchloride (CH_2Cl) to the $-\text{CH}_2\text{Q}^+ \text{Cl}^-$ group, due to diffusional limitation of amine/substrate. Ultimately, there may be a reduction of catalytic activity and it is quite common that the reactivity of the triphase catalyst depends on hydrophilicity, which is an indirect measure of the extent of quaternization. It is also very clear that the influxed $-\text{CH}_2\text{Cl}$ group in polymer network of the beads (as in type 2) will only be a waste. Even if the active-site group located inside the polymer matrix was quaternized, there are further hurdles for the participation of active sites in reactions. That is, when it was employed in organic reactions, participation of active sites is difficult due to diffusibility of organic substrate, intraparticle diffusion of reactants from the surface of the particles to the active sites within the polymer matrix, and diffusion of the products from inside the catalyst to the bulk liquid.

From the preceding arguments, it is clear that only the active region near the bead surface is effectively involved in the chemical reaction; hence, it is worthwhile to mention here that the "surface-enriched with active-sites" bead-shaped catalyst (type 1) is trustworthy in catalytic action, particularly in maximum utilization of $-\text{CH}_2\text{Cl}$ group.

In order to increase the number of active sites on the surface of beads, we normally carried out

the suspension polymerization of St and DVB and then the functional monomer (VBC) was added after 12 h to the partially polymerized copolymer of St/DVB. Initially, sufficient amounts of DVB and styrene undergo copolymerization and after the partial polymerization of St/DVB (up to 12 h), due to delayed and slow addition of VBC, a portion of monomer may copolymerize with St/DVB and the remaining (major) portion was chemically grafted onto the surface of poly(St/DVB) particles. The homopolymerization of VBC due to delayed introduction and the chemical grafting of VBC onto the surface of St/DVB particles have been cross-checked by precipitation techniques.

Grafting of VBC in St/DVB

Because of delayed addition (after 12 h) of functional monomer in type 1 beads, there is the chance for the formation of homopolymers of VBC due to the nonavailability of living radicals of St/DVB and to the availability of free radical initiator (AIBN). To clarify this, the mother liquor (first-filtered solution from the polymer reaction mixture) of polymer solution was subjected to precipitation process with an excess of nonsolvent, that is, methanol. But no precipitate was obtained with it, confirming the absence of the homopolymerization of functional monomer (VBC). Further, 2 g of dried copolymer beads (170–200 mesh size) and 75 ml toluene [an excellent solvent for poly(VBC)] were transferred to a 100-ml conical flask, which was stirred continuously using magnetic pellets for 3 days at room temperature; the resulting toluene extract was poured into ex-

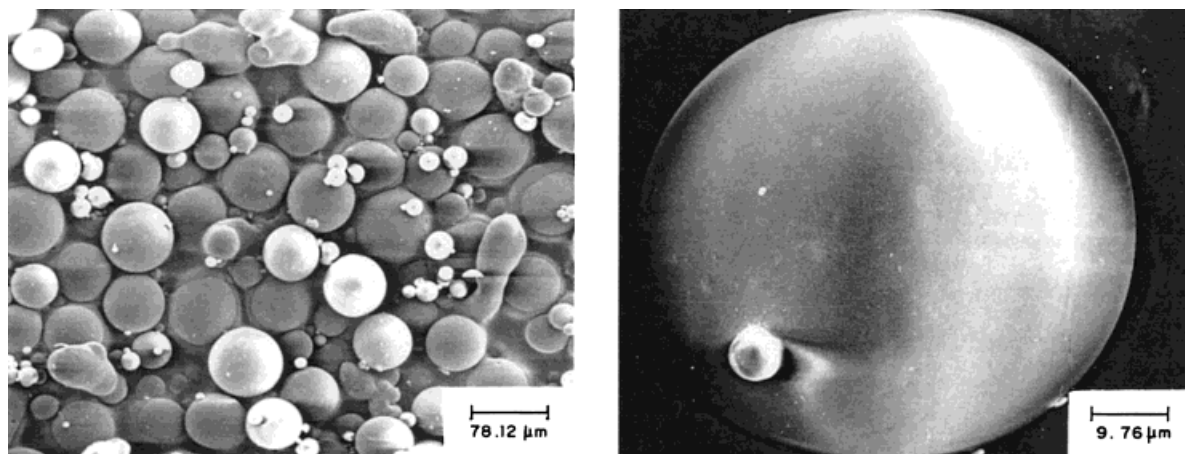


Figure 1 Scanning electron micrograph of the conventional catalyst (type 2): (a) overall view; (b) magnified view of the single bead.

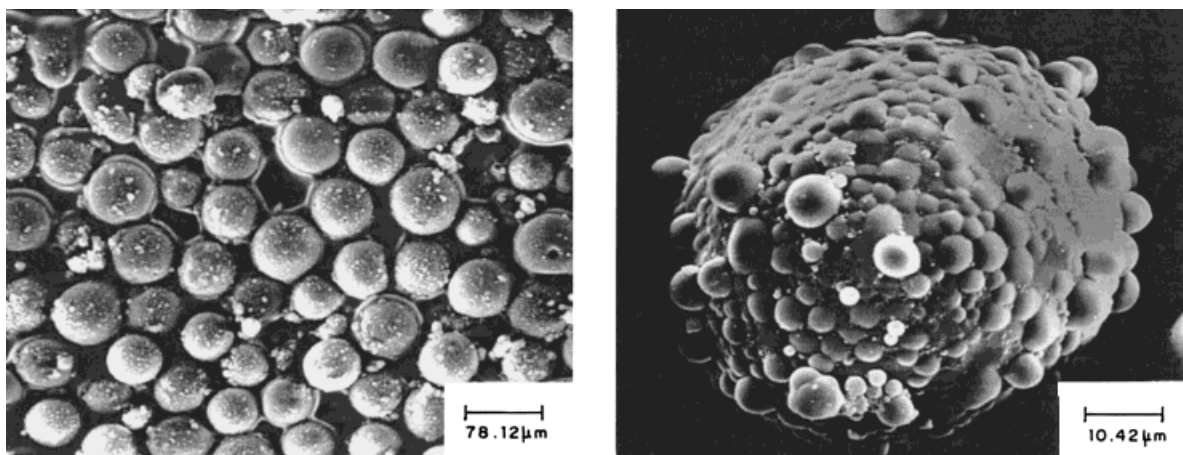


Figure 2 Scanning electron micrograph of the SE-PSPTC (type 1) catalyst: (a) overall view; (b) magnified view of the single bead.

cess methanol for the precipitation of any extracted physisorbed VBC on St/DVB. Here, too, no precipitate was obtained, proving the chemical grafting of VBC onto the surface of St/DVB; thus, the delayed introduction of VBC (type 1) may be an appropriate technique to bring most of the $-\text{CH}_2\text{Cl}$ groups on the surface.

Images of Scanning Electron Microscope and EDAX Observations

The surface morphology of type 1 [Fig. 1(a) and (b)] copolymer beads contains a large number of attached nodules in marked contrast to the relatively smooth surface of type 2 [Fig. 2(a) and (b)]. The attached nodules are the result of the chemical grafting of poly(VBC) onto the particles of

St/DVB, which is due to the delayed introduction of VBC into the partially copolymerized St/DVB system; the primary poly(St/DVB) network has already been formed. Therefore, the added VBC molecules (after 12 h) must chemically graft onto the surface of partially polymerized beads of St/DVB and so the surface is rich in active-site ($-\text{CH}_2\text{Cl}$) grouping, which appears as nodules in SEM images. However, in the case of type 2 polymer beads, nodules do not form on the surface, since (1) VBC and DVB are more reactive than St and (2) the monomer responsible for nodule (VBC) formation was mixed homogeneously with supporting monomer. In EDAX analysis, the peak intensity (Fig. 3) of surface chlorine in type 1 catalysts was found to be greater than that of type 2 catalyst, which firmly supports the surface en-

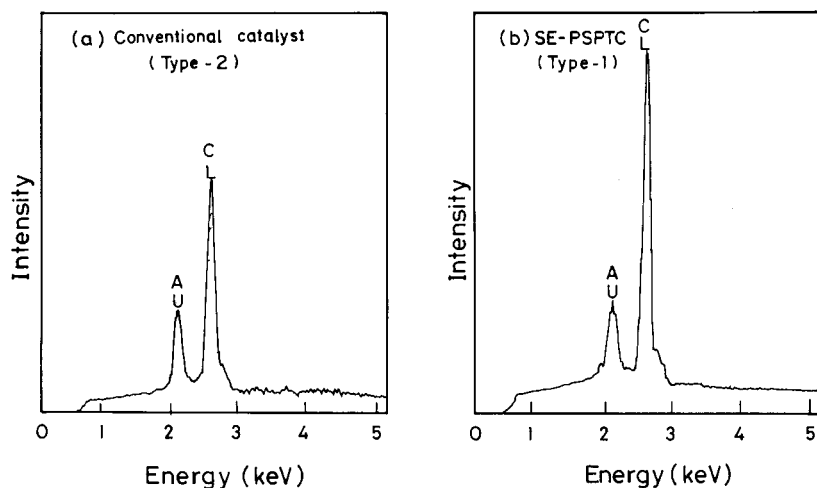


Figure 3 EDAX spectrum: (a) conventional catalyst (type 2); (b) SE-PSPTC (type 1).

richment of benzyl chloride group and the appearance of gold signal in the spectrum (due to its coating).

FTIR Inference

The FTIR spectra of type 1 and type 2 catalysts are shown in Figure 4. Although both spectra are superimposable with respect to peak position, the intensities of characteristic peaks for type 1 catalyst exhibit notable differences compared to type 2 catalyst. For convenience, the characterization peaks such as C—N stretching (quaternary ammonium group) and C—Cl stretching ($-\text{CH}_2\text{Cl}$) of both the catalysts are given in Figure 3. The absorbance of C—N stretching peaks at 1158 cm^{-1} in type 1 catalyst (0.84) are found to be more intense than the type 2 catalyst (0.16) and also the absorbance of C—Cl stretching was observed at 710 cm^{-1} ,^{18,26} which decreases in type 1 (0.09)

and increases in type 2 (0.69) and which is the direct measure of quaternization of $-\text{CH}_2\text{Cl}$ grouping. This lends support for the active-site enrichment in type 1 catalyst, because more quaternization is possible if most of the $-\text{CH}_2\text{Cl}$ grouping is grafted onto the surface.

Electron Spectroscopy for Chemical Analysis (ESCA; XPS)

It is well known that the ESCA is among the most powerful tools to determine the surface element, either quantitatively or qualitatively, of the samples. The unquaternized copolymer beads of both types were taken for quantitative analysis by maintaining the depth of information limit at about 30 \AA . Since the copolymer beads are prepared from styrene, VBC, and DVB, they must be composed of carbon (C), hydrogen (H), and chlorine (Cl). The line positions from Al K X-rays are

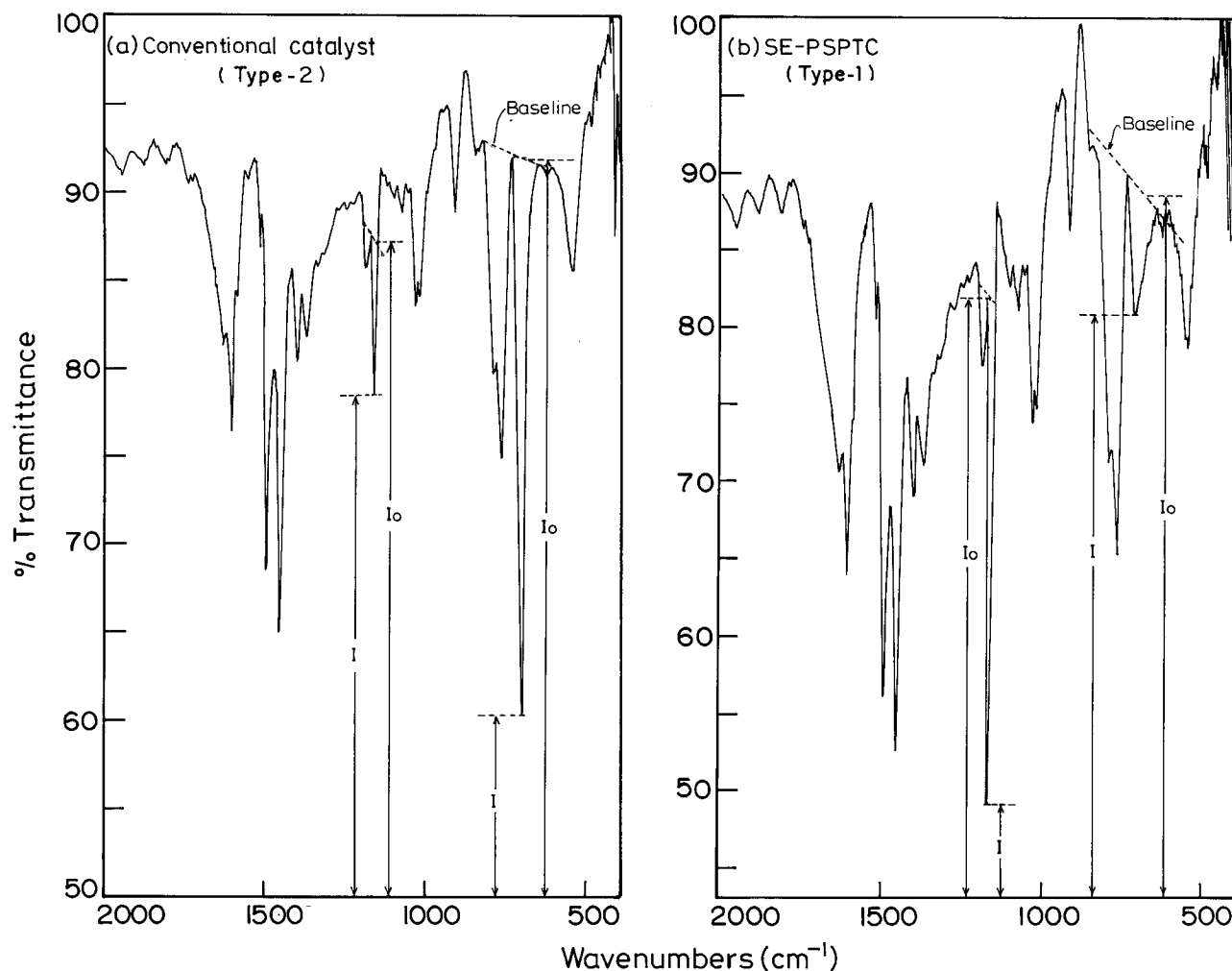


Figure 4 Comparative FTIR spectrum of type 1 and type 2 catalyst.

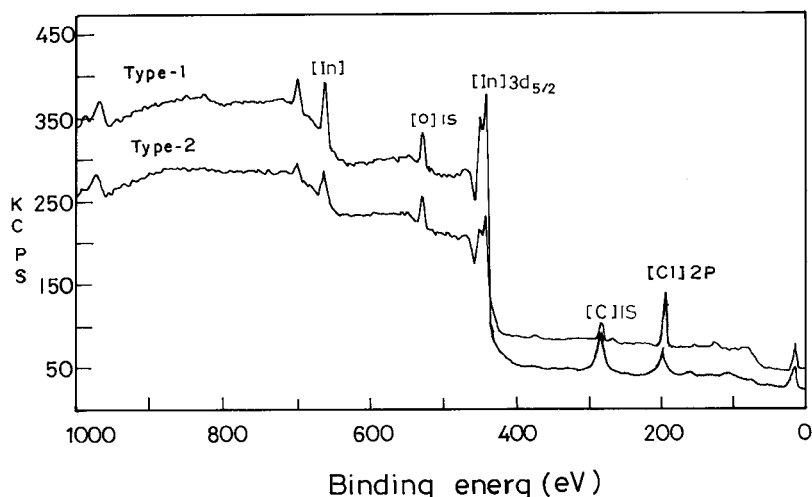


Figure 5 Comparative ESCA survey spectrum for the type 1 and type 2 polymer beads.

as follows: C 1s 287, Cl 2p_{3/2} 199.9, Cl 2p_{1/2} 201.5 eV.²⁷⁻²⁹

Figure 5 is the overall survey scan of ESCA for both samples and it reveals that the elements carbon, chlorine, indium, and oxygen are present on the surface of beads. The XPS peaks relating to the background of indium foil (i.e., 3s, 3p, 3d) are identified at the binding energy (BE) of around 828, 664–704, and 445–453 eV. The XPS peak relating to C at 287 eV agrees well with the literature findings. The characteristic covalent chloride (active site) in type 1 and type 2 is observed with the BE value of 199 eV. Figure 6 clearly shows the quantum of carbon and chlorine

present on the surface. It is well known that the count rates of photoelectrons' intensity relating to an XPS peak are the direct measure of the quantity of the concerned element present in the material³⁰; hence, the peak intensities of C 1s in terms of photoelectron count rates (KCPS) in type 1 is 15.5k, which is less than the intensities of C 1s of type 2 (25k), whereas the chlorine 2p peak in type 1 is 15k, which is absolutely greater than type 2 (8k). More intensities of surface carbon in type 2 were attributed to carbons of St, DVB, and VBC (due to homogeneous mixing of all three monomers), whereas the type 1 outer layer corresponds to VBC carbon only (because of surface

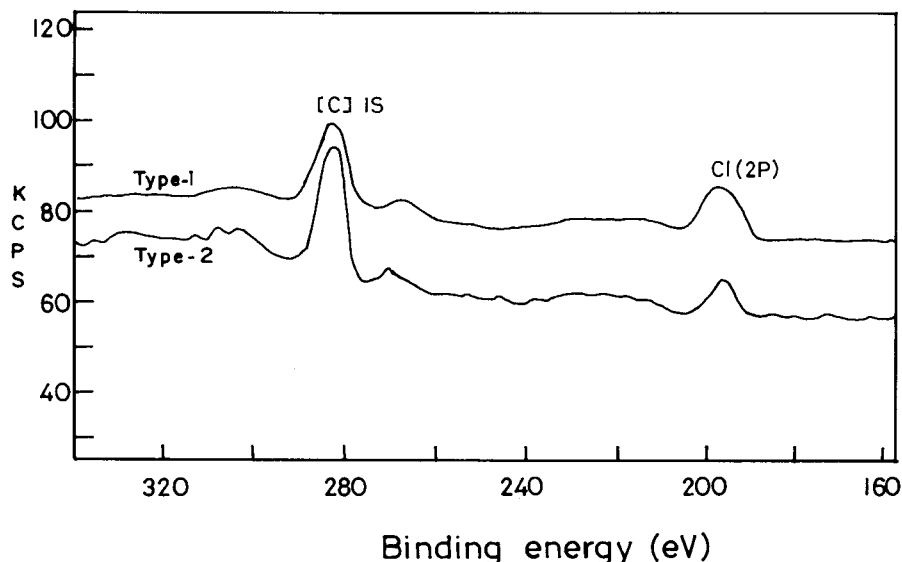


Figure 6 Magnified ESCA spectrum of carbon and chlorine.

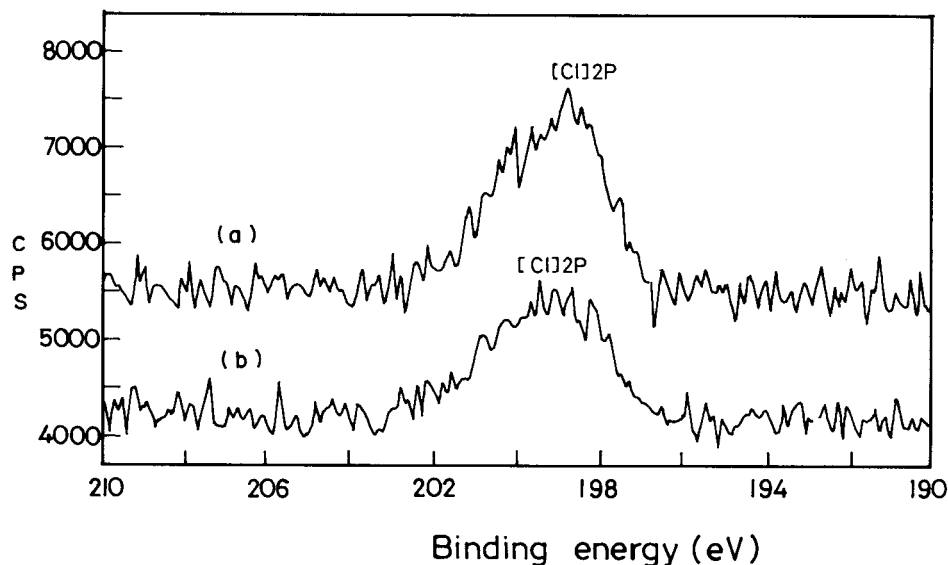


Figure 7 Magnified ESCA spectrum of chlorine only.

grafting) and subsequently the amount of chlorine is greater in type 1 than in type 2. This inverse proportion of chlorine and carbon clearly confirms the enrichment of chlorine in type 1. This is also supported by the fact of the magnified peak (Fig. 7) of the chlorine region, where it is clearly evident that the intensities of Cl 2p relating to type 1 (2420 CPS) are much more than the intensities of Cl 2p corresponding to type 2 (1250 CPS). The deconvolution (Fig. 8) of the chlorine peak shows two peaks with binding energies of 198.6 (Cl $2P_{3/2}$) and 200.4 (Cl $2P_{1/2}$) eV and this

finding agrees with the literature^{26,27} fingerprint values of the same. The doublet of covalent chlorine was imputed to spin-orbit interaction because the Cl 2p level has split in the form Cl $2P_{1/2}$ and Cl $2P_{3/2}$.

To further establish our findings, the Eclipse software was applied to calculate the percentage of carbon and chlorine on the surface (Fig. 5). The calculated results were 26% of covalent chloride and 36% of carbon available on the surface of type 1; similarly, 14 and 54% of covalent chlorine and carbon were present on the surface of type 2. The

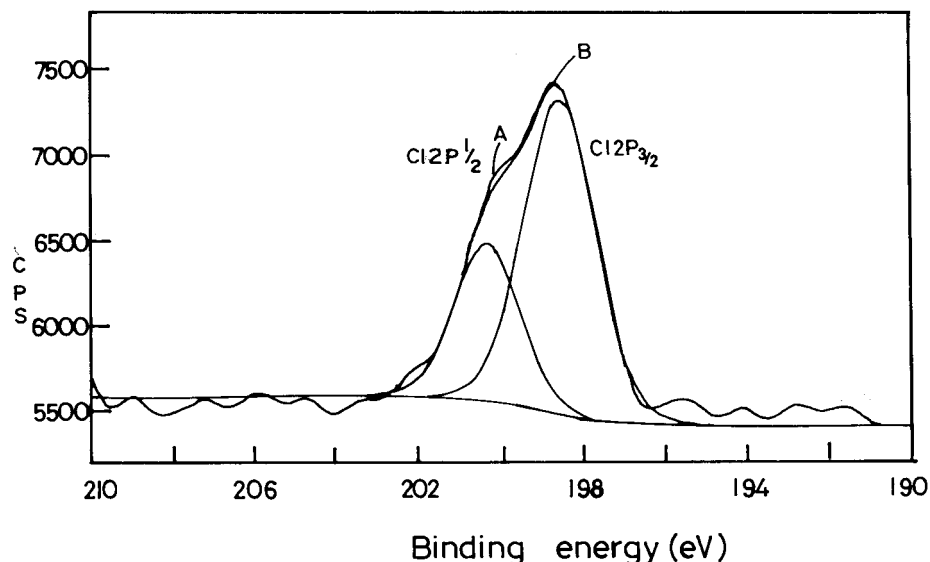


Figure 8 Deconvolution of ESCA spectrum of chlorine.

remaining percentages were indium and oxygen. The overall observation of surface chlorine in both types of beads obtained from software methods explains that type 1 is always predominant with respect to percentage of chlorine on a par with the intensity measurements in terms of KPCS; hence, type 1 has more quaternizing residue on the surface, resulting in higher product yield in organic reactions.

Effect of Accessible Hydrophilicity and Catalytic Activity

The ionic chloride content of these two different catalysts was found by the Volhard technique. The type 1 catalyst has 4.73 m eq g^{-1} and type 2 has 2.29 m eq g^{-1} of quaternized chloride. These two kinds of quaternary onium salts were employed as phase transfer catalysts to carry out the alkylation of phenylacetone with 1-bromobutane. The observed pseudo-first-order rate constant values (Table I) for both catalysts reveal that the type 1 catalyst has a twofold increase in activity over that of type 2. The rate constants of recovered and regenerated yields for both catalysts also follow the same trend. The increased rate constant of type 1 indicates the nonoperativity of diffusional limitation, whereas a decreased rate constant in type 2 would strongly confirm the operation of diffusional limitation. It means that the characteristic hydrophilicity of type 1 is greater than that of type 2. On the basis of a greater amount of ionic chloride and increased rate constant, type 1 further demonstrates active-site enrichment on the surface.

CONCLUSIONS

Polymer-supported catalysts with active-site-enriched surface were prepared by suspension polymerization technique. The surface morphology of the catalysts was observed by scanning electron microscope. The nodules attached on the surface in type 1 catalyst are due to grafting of active-site monomer onto the surface; hence, type 1 catalyst has a nonhomogeneous surface in contrast to the smooth surface of type 2 catalyst. From the EDAX spectrum, the increased peak intensity of chlorine for type 1 reveals that most of the active species are on the surface. In FTIR spectra, the peak intensity of C—N stretching is greater in type 1 than in type 2 catalyst, which is possible only if most of the $-\text{CH}_2\text{Cl}$ group is found on the surface. The ESCA analysis of unquaternized poly-

mer beads reveals that type 1 contains, respectively, 26 and 36% of surface covalent chlorine and carbon; similarly, type 2 was found to have 14 and 54% of chlorine and carbon contents. This opposite trend of more chlorine and less carbon in type 1 catalyst confirms the chlorine enrichment on the surface compared with its counterpart, type 2 catalyst. The quantum of ionic chloride and the observed rate constants also prove the same.

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REFERENCES

- Balakrishnan, T.; Ford, W. T. *J Org Chem* 1983, 48, 1029.
- Balakrishnan, T.; Hari Babu, S.; Shabeer, T. K. *J Polym Sci Part A Polym Chem* 1993, 31, 317.
- Balakrishnan, T.; Hari Babu, S.; Perumal, A. *J Polym Sci A: Polym Chem* 1990, 28, 1421.
- Montanari, F.; Tundo, P. *Tetrahedron Lett* 1979, 52, 5055.
- Montanari, F.; Tundo, P. *J Org Chem* 1981, 46, 2125.
- Tomoi, M.; Yanai, N.; Shiiki, S.; Kakiuchi, H. *J Polym Sci Polym Chem Ed* 1981, 22, 911.
- Capillon, J.; Richard, A.; Adubert, R.; Quivoron, C. *Polym Bull* 1984, 13, 185.
- Chiellini, E.; Solaro, R.; Antone, S. D. *Makromol Chem Suppl* 1981, 5, 82.
- Ford, W. T. in *Polymeric Reagents and Catalysts*, Ford, N. T., ed.; ACS Symposium Series 308; American Chemical Society: Washington, DC, 1992; 229.
- Ahmed, A.; Sherrington, D. C. *Chem Rev* 1981, 81, 557.
- Giannini, U.; Mayer, A.; Longi, P.; Susa, E.; Davoli, V.; Deluca, D.; Leccese, A.; Pricca, A. *Ger Offen* 2 1971, 125, 107.
- Kinkelin, E.; Fink, G.; Bogdavonic, B. *Makromol Chem Rapid Commun* 1985, 7, 85.
- Regen, S. L. *J Org Chem* 1977, 42, 875.
- Regen, S. L. *Angew Chem Int Ed Engl* 1979, 18, 421.
- Chu-Chou, S.; Shan-Weng, H. *J Appl Polym Sci* 1990, 39, 1665.
- Balakrishnan, T.; Ford, W. T. *J Appl Polym Sci* 1982, 27, 133.
- Ford, W. T.; Tomoi, M. *Adv Polym Sci* 1984, 55, 49.
- Hong, L.; Ruckenstein, E. *Polymer* 1982, 33, 1968.
- Hartley, E. R. *Supported Metal Complexes*; Reidel: Dordrecht, 1985; Chapter 4, pp 118–133.

20. Reilley, C. N.; Everhart, D. S.; Ho, F. F. L. in *Applied Electron Spectroscopy for Chemical Analysis*; Windawi, H.; Ho, F. F., Eds.; Wiley: New York, 1982; p 122–190.
21. Tang, S. C.; Paxson, T. E.; Kim, L. *J Mol Catal* 1980, 9, 313.
22. Ruckenstein, E.; Hong, L. *J Catal* 1992, 136, 378.
23. Tomai, M.; Ford, W. T. *J Am Chem Soc* 1980, 102, 7140.
24. Tomai, M.; Ford, W. T. *J Am Chem Soc* 1981, 103, 3821.
25. Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963.
26. Dyer, J. R. *Application of Absorption Spectroscopy of Organic Compounds*; Prentice–Hall: Englewood, Cliffs, NJ, 1987.
27. Adem, E. V. G. *Scientific XPS Hand Book*, 1981.
28. Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Hand Book of X-ray Photoelectron Spectroscopy*; Perkin-Elmer; Minnesota, 1976.
29. *Fissions Instruments Surface Science, XPS and AUGER Hand Book*, 1985.
30. Riggs, W. M.; Parker, M. J. *Methods of Surface Analysis*; Czanderna, A. W., Ed.; Elsevier: Amsterdam, 1975; Chapter 4, p 106.