A Modified Method for the Synthesis and Characterization of a Novel Surface-Enriched (with Active Site) Polymer-Supported Phase Transfer Catalyst Using Vinyltoluene as a Functionality and Its Catalytic Efficiency in Dichlorocarbene Addition to Olefines—A Kinetic Study

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ABSTRACT

A modified method with respect to an earlier conventional procedure was successfully attempted and we now report the new procedure for the synthesis of surface-grafting technique by the delayed addition of inexpensive vinyltoluene (VT) functionality to the partially polymerized supporting monomers viz., styrene (St) and divinylbenzene (DVB) via suspension polymerization. The resulting copolymer beads containing surface-enriched with methyl group were converted into a catalyst by chlorination followed by a quaternization process. Two groups (I and II) of SE-PSPTC beads were prepared by fixing the crosslinking amount (DVB) as 2% and 6%, respectively, 25% of VT as a common active site functionality and the rest of the contribution was styrene. Each group contains six different catalysts based on the concentration of active sites on the surface which in turn depends upon the partial polymerization time (PPT) of St/DVB i.e., 0, 3, 6, 9, 12, and 15 hrs. These two different groups and 6 different catalysts categories in each were prepared with

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the objective to learn the influence of higher/lower crosslinking in the process of surface-grafting of poly(VT) on poly(St/DVB) and to determine the optimized partial polymerization time to bring the maximum active site on the surface. The level of enrichment of an active site of all the catalysts were determined through [chloride], FT-IR, SEM, EDAX, and ESCA analyses. The gradual increase of [chloride], C-N peak intensity from FT-IR, rough surface/nodules concentration from SEM, % of surface chloride from EDAX, decreasing/increase trend of surface carbon/surface chloride in ESCA analyses starting with 0 VT to 15 VT irrespective groups, confirms the gradual increase of active site on the surface beads based on the PPT. The results of [chloride], spectral analyses and the rate constants of all the catalysts in dichlorocarbene addition to various olefines ensure that 9 VT-SE-PSPTC was the best catalyst beads in both the groups due to its two-fold enhancement rather than the conventional catalyst (0 VT) of both groups although we had added the same amount of VT in both preparations.

INTRODUCTION

The concept "Phase-transfer Catalysis" has achieved wide recognition and acclaim because of its ability to carry out the reactions between two immiscible reactants. The use of a soluble form of onium and other related phase-transfer catalysts in biphase catalytic reaction always encounters separation problem since its introduction by Jerrouse[1], although it is considered as inexpensive and attractive. As an alternative, insoluble form of polymer-supported phase transfer catalyst (PSPTC) was reported by Regen[2] using immobilization of active moiety (triethylamine) on the crosslinked polymer and thereafter its scope and limitations of this "triphase catalyst" are well exploited. Later on PSPTC studies reported by Montanari et al.,[3–5] Brown et al.,[6] Ohtani et al.,[7] Chaudhari et al.,[8] Marchoni et al.,[9] Ford et al.,[10,11] and Balakrishnan et al.[12–15] paved the way for synthesizing different organic compounds from immiscible reactants. So far, in the field of PSPTC, the research is devoted to developing a new polymer-support to enhance the catalytic reaction rate more effectively[16,17] and to examine the influence of factors like the structure of active sites,[18–19] particle size of the catalyst,[20,21] structure and degree of crosslinking.[22–24]

However, in the polymer-supported bead shaped phase transfer catalysts, the effects of the internal and external molecular structure of the catalyst had played a vital role on the reaction rate which has been rarely discussed in the literature. According to Regen,[25] the overall rate in triphase catalysis was influenced by a diffusional limitation, mass transfer,r and chemical reaction. Tomoi et al.[21,22] pointed out that the resistance of particle diffusion had controlled the chemical reactions. As a result of early findings in bead-shaped PSPTC, if active sites are available on the surface, it may turn out to be a major factor in deciding the rate-limiting step of the reaction. Studies[26] are also available in the literature for the preparation of polymer-supported bead-shaped catalyst using hydrophilic polymer-support viz., poly(ethylene glycol)

methacrylate for the synthesis of solid phase hydontoins. Svec et al.[27] reported poly(2,3-dihyroxypropylmethacrylate-co-ethylenedimethylacrylate) bead-shaped catalyst for separation of hydrophilic oligomers more effectively. Studies are also available for the functionlization of monomers containing $-COOH^{[28,29]}$, $-CONH_2^{[30]}$, $-CH_2NH_2^{[31,32]}$ functionality which in turn are to be used as a base for catalytic sites even with/without spacer groups. The grafting of active site functionality on the surface of beads containing styrenic double bonds were also attempted and reported[33], wherein the grafting process may be efficient with only a limited amount of the residual double bonds 20 to 30%. Though there were a number of studies on the preparation of microporous bead-shaped insoluble PTC and surface-enrichment of the active site using hydrophilic functional monomers and grafting of functionality through styrenic double bonds are in the literature, there is no report on the study of bead-shaped surface-enriched (with active site) polymer-supported phase-transfer catalyst (SE-PSPTC) by suspension polymerization technique. Furthermore, in our thorough literature survey on the preparation of PSPTC, we find that by and large vinylbenzylchloride (VBC) has been used traditionally as a precursor for functionalization. We have also reported[12] a similar type of PS-PTC beads using VBC as a functionality. Since VBC is a costly monomer, any polymer scientist would like to replace that and introduce an alternative inexpensive functionality. As an alternate method, Mohanraj et al.[34] reported the preparation of insoluble PSPTC beads using vinyltoluene (VT) as a functional monomer. However, in their studies, they have not concentrated on the location of the active site. As a result, those conventional catalysts may render diffusional limitation into and out of the polymer-matrix during a chemical reaction. According to Balakrishnan et al.,[35] if the functional monomer (VBC) is added simultaneously to the supporting monomers, then the majority of the reactive functionalities is buried/influxed inside the bead containing supporting-monomers in the network of poly(St/DVB) and also an active site available inside remains unutilized In the same way, with the Mohanraj et al.[34] method, the bead has been initially prepared by adding the functional monomer vinyltoluene along with the supporting monomers St/DVB. Therefore, we firmly suspect that because of a simultaneous addition of VT along with the St/DVB, the major portion of VT may be embedded inside the poly(St/DVB) network. When these conventional beads were made into the catalysts through conversion of VT functional group ($-CH_3$) via chlorination ($-CH_2Cl$) and quaternization (CH_2/Q^+Cl^-), due to diffusional limitation of chlorinating agent/ quaternizing amine substrate, the $-CH_3$ group present inside the bead may not be available as such for conversion and becomes waste. Even if the inside $-CH_3$ is effectively chlorinated/quaternized, when it was employed as a catalyst in a reaction involving bulky substrate, again dislodging of active sites occurred due to a diffusibility of organic substrate/relevant product inside or out of the bead matrix(desorption).

In this study, we report a modified method for the synthesis of bead-shaped "surface-enriched (with active site) polymer-supported phase transfer catalyst (SE-PSPTC)" using vinyl toluene as a functionality via suspension copolymerization technique. The determination of an active site on the surface and efficiency of the catalysts have been studied by various surface characterization techniques and chemical reaction method.

EXPERIMENTAL

Materials

Styrene (Fluka), Divinylbenzene (Fluka) and Vinyltoluene (Fluka), were used as received without the removal of inhibitors. Poly(vinyl alcohol) (Fluka) with Mwt.72,000 and gelatin (AR,BDH) combination was used as the suspension stabilizer. Boric acid, triethylamine, acetonitrile and methanol (S. D. Fine, AR) were used as is without further purification. AIBN (Kochlight, USA) was recrystallized from ethanol. 1-octene (Fluka), cis-cyclooctene (Fluka), cyclohexene (Fluka), chloroform (SRL,AR), sodium hydroxide (E.Merck) were used as such in the reactions.

Instrumentation

FT-IR absorption spectra was recorded with a Nicolet 20DXB-FTIR spectrophotometer using the KBr pellet. Surface morphology and semi-quantitative analyses of an active site of the SE-PSPTC were analyzed using a JEOL JSM-35 scanning electron microscope (SEM) and its interfaced unit viz. EDAX (Energy dispersive X-ray analysis) instrument of tracor northern TN-5400, respectively. Quantitative determination of the active site on the surface of the each catalysts was studied using a VG ESCA (Electron spectroscopy for chemical analysis) MK200X XPS analyzer. Kinetics of the catalyzed addition reactions were quantitatively analyzed by a gas chromatograph (Varian-3700 interfaced with vista CDS 401) with flame ionization detector. The column used for the product analysis was 10% SE-30, chrom WHP 80/120, 3MX 1/8, stainless tube.

Typical Method for the Preparation of Bead-Shaped Crosslinked Polystyrene Enriched with Methyl Group on the Surface by the Suspension Polymerization Method

As a first step of the catalyst preparation process, crosslinked polystyrene beads with surface-enriched with methyl group were prepared by fixing the crosslinking (i.e., divinylbenzene) ratio as 2% (group I) and 6% (group II), respectively and functional monomer(i.e., VT) as 25% as common and the rest of the monomer is styrene. Each group contains 6 types of beads based on their partial polymerization time (PPT) of St/DVB. The first group of beads consisting of 6 different types due to its PPT of St/DVB and the amount of enrichment of methyl groups poly(VT) on the surface of poly(St/DVB) particles were prepared by using the organic phase 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 poly(vinylalcohol) were thoroughly dissolved in 35, 60, and 130 ml of double distilled hot water (50℃), respectively. Then these solutions were mixed together at room temperature. The dissolved poly(vinyl alcohol) maintains the viscosity of the medium. The pH of the mixed solution was adjusted to 10 with a digital pH meter(Model L1120 Elico) using a 25% aqueous sodium hydroxide solution and 0.1 g sodium nitrite to maintain the conformation of gelatin. The aqueous phase became clear only after adjusting the pH to 10. It was then transferred to a 500 ml

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threenecked RB flask equipped with an overhead mechanical stirrer and reflux condenser. Nitrogen was passed continuously and the temperature was fixed at 50°C. After half an hour, maintaining the above condition, the organic phase containing 3.3 g (2%) divinylbenzene, 58.57 g of styrene and 0.4125 g of AIBN was thoroughly mixed and added to the reaction flask. The blade level of the stirrer was adjusted so that the tips were in a organic phase and most of the blade in an aqueous phase. Subsequently, the thermostat temperature was increased to 70°C and the stirring speed was maintained at 400 rpm using a tachometer. The polymerization of styrene and divinylbenzene was allowed to proceed up to 3 h (partial polymerization time (PPT)), and then the surface-grafting functional monomer (vinyltoluene, 20.62 g (25%)) was added dropwise to the reaction flask through an addition funnel; the duration of the addition was maintained at 1 h and the copolymerization was allowed to go to completion for 48 h, which includes the partial polymerization time of St/DVB (Sch. IB).

The copolymer beads having surfaceenriched with poly(VT), were filtered through a Buchner funnel and washed with hot water and cold methanol repeatedly until the wash solution did not turn cloudy upon the addition of water. It was then dried at 60°C in a vacuum oven for 2 days. Since those beads were obtained by adding the functional monomer (VT) after allowing the 3 h partial polymerization of St/DVB, we labeled as 3 VT. Similarly, under the same conditions and quantities of aqueous and organic phase, the other types of beads were also prepared by adding a functional monomer after the partial polymerization time of St/DVB for 6 h (6 VT), 9 h (9 VT), 12 h (12 VT) and 15 h (15 VT).
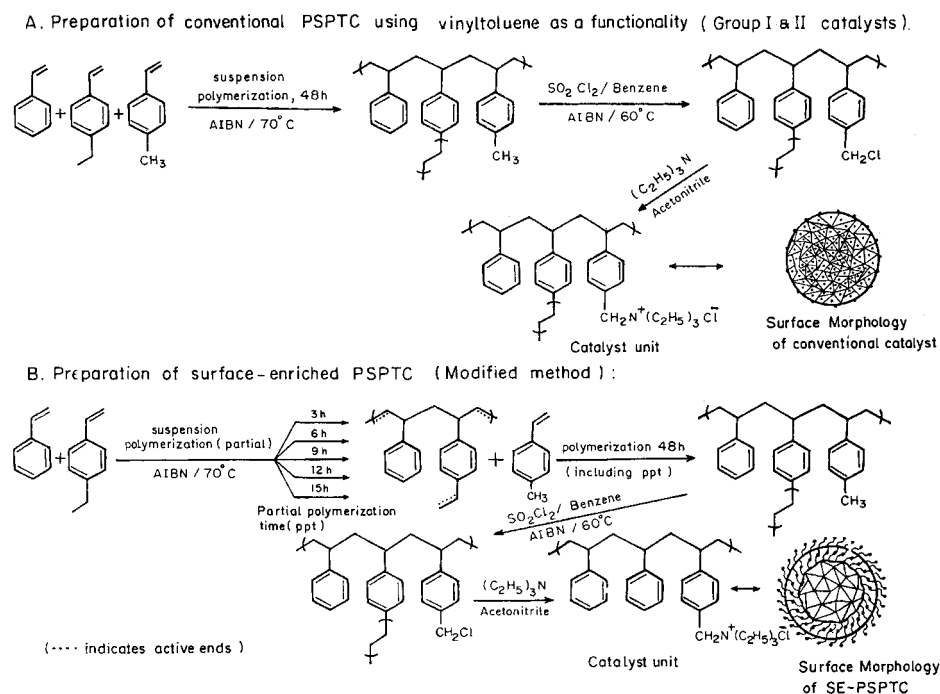
Scheme 1.

In the case of the conventional method[34], the functional monomer VT was added along with supporting monomers without allowing partial polymerization of St/DVB (Sch. 1A) and thereby it was labeled as 0 VT (PPT = 0 h). Similarly, the group II type beads containing the same 6 different types viz. (0 VT, 3 VT, 6 VT, 9 VT, 12 VT and 15 VT) were also prepared by following the same methodology/strategy adopted for the preparation of group I types of beads. The only variation for the preparation of group II type beads was the amount of crosslinking (DVB) used. That is, the DVB used for this group II was fixed at 6% (9.9 g) and as we mentioned earlier, the amount of VT was 25% (20.62 g) and as usual, the rest of the amount is styrene (51.97 g). Also, the volume and amount of other chemicals used for the preparation of aqueous phase were also the same as that of group I. This group II beads were prepared by aiming to know about the degree of surface-grafting of Poly(VT) on poly(St/DVB) beads under higher crosslinking. These two groups (I and II) of dried polymer beads were sieved into different mesh sizes using a ROTAP testing sieve shaker (W. S.Tyler Company, Cleveland, Ohio).

Chlorination of Crosslinked Polystyrene Beads with Surface Enriched with Methyl Group

The second step for the preparation of the catalyst was the chlorination[34] of crosslinked polystyrene beads with surface enriched with a different concentration of methyl group obtained from both the types (group I and II). From each type of both the groups, representative mesh sizes viz., $-80 + 100$, $-100 + 120$, and $-120 + 140$ beads were subjected to a chlorination reaction (Sch. 1 A, B) individually by placing 5 g polymer beads in a 250 ml flask, 50 ml of benzene, and 70 mg of AIBN were added. The mixture was stirred at room temperature under nitrogen atmosphere for about 60°C. A solution of 10.5 ml of SO_2Cl_2 in 10 ml of benzene and 150 mg of AIBN were added dropwise through an addition funnel over a period of 1 h.The reaction mixture was stirred for another 2 h, cooled to room temperature and cold methanol was added with stirring. The mixture was filtered and the chlorinated beads were washed with methanol, dichloromethane, and methanol. The resulting crosslinked polystyrene beads with surface-enriched with benzyl chloride group ($-CH_2Cl$) were dried in vacuum at 70°C for about 24 h. The FT-IR spectrum of chlorinated beads shows the characteristic peaks at 1265 cm^{-1} for methylene group ($-CH_2-$) and 710 cm^{-1} for C–Cl stretching which confirms the chlorination of methyl group.

Preparation of Bead-Shaped Surface-Enriched (with Active Site) Polymer-Supported Phase Transfer Catalyst (SE-PSPTC)

The third step, viz. the preparation of catalyst, is carried out as detailed below: Representative mesh sizes of crosslinked polystyrene beads with surface-enriched with benzylchloride groups obtained from different PPTs of group (I and II) were directly converted to a catalyst by reacting with triethylamine[13] (Sch. 1). 5 g of a representative mesh size of polymer beads, 150 ml of acetonitrile and 30 ml of triethylamine were placed in a 250 ml two-necked flask. The mixture was purged with nitrogen, deaerated under

vacuum and the entire setup was placed in an oil bath over a magnetic stirrer and the mixture was refluxed at 70°C for 3 days with a continuous sweep of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with acetonitrile and methanol followed by drying under vacuum at 60°C. The resulting dried beads of both the groups with different PPTs is the "surface-enriched (with active site) polymersupported phasetransfer catalyst (SEPSPTC)." The chloride ion concentration of both the I and II group catalysts were estimated as per the procedure[36,37] (Table 1).

Preparation of the Samples for Various Surface Characterization Techniques

The FT-IR specimen for both the group I and II catalysts were prepared in the form of pellets by following the disc technique and was employed for quantitative analysis of characteristic peaks. Since we were using this technique as a semi-quantitative study, adequate care has been taken to prepare the pellets. Known weights of KBr and test substance of different SEPSPTC's (1:1 ratio) were taken for pellet making. The thickness of the pellets of catalysts from 0 VT to 15 VT-SE-PSPTC of both groups of the representative mesh size were maintained uniformly using a dial micrometer. That is, the thickness of pellets disk were measured at several points on the surface through a dial micrometer and then employed to analysis. Since our intention of this analysis was to assess the best SE-PSPTC having a more active site on the surface from each groups, the characteristic peak intensity of CCl stretching at $710 \, cm^1$ (i.e., CH_2Cl group obtained via chlorination) and CN stretching at $1158 \, cm^1$ (obtained via quaternization $CH_2N^+(C_2H_5)_3$-Cl) were measured by a base line method technique (Fig. 1). We had run the FTIR spectrum in transmittance mode. In order to calculate the absorbance of characteristic bands, the height of incident radiation energy I_o and height of its transmittance. I were measured by drawing a straight line tangent to the characteristic band of CCl stretching. Similarly, the value of I_o and I for CN stretching was also measured. The value of $\log(I_o/I)$ for each band gives their respective absorbance which is a direct measure of active site concentration of the characteristic peaks. The calculated absorbance values of all the types of catalysts for I and II groups are given in Table 2.

Table 1. Estimation of chloride ion concentration for the first and second group 0 VT's and SE-PSPTCs.

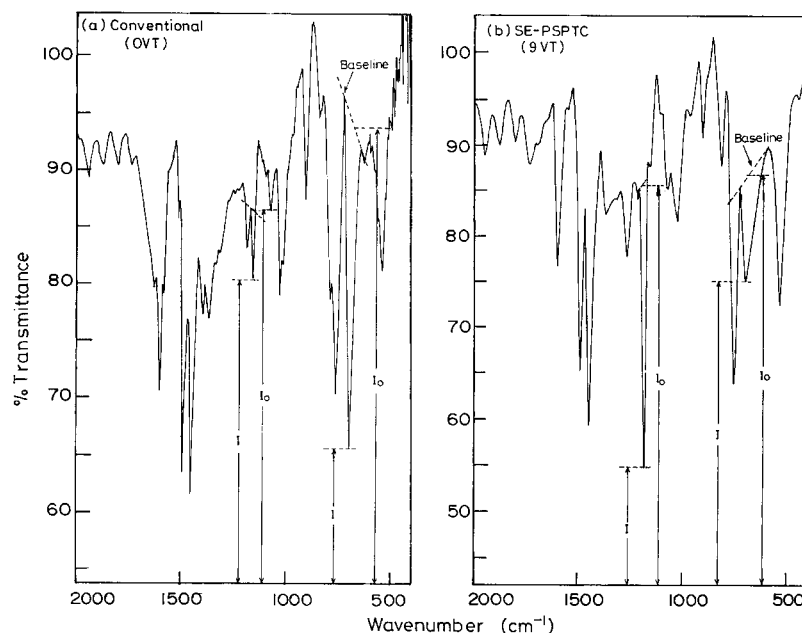| Name of the catalysts	Group I catalysts			Group II catalysts		
	$-80 + 100$ m.equ.g^{-1}	$-100 + 120$ m.equ.g^{-1}	$-120 + 140$ m.equ.g^{-1}	$-80 + 100$ m.equ.g^{-1}	$-100 + 120$ m.equ.g^{-1}	$-120 + 140$ m.equ.g^{-1}
0VT	1.19	1.39	1.586	1.09	1.20	1.48
3VT	1.38	1.41	1.921	1.31	1.39	1.72
6VT	1.70	2.12	2.46	1.64	2.07	2.40
9VT	2.42	2.84	3.20	2.30	2.76	3.02
12VT	2.63	2.95	3.24	2.42	2.79	3.07
15VT	2.66	2.96	3.27	2.50	2.81	3.11

Figure 1. Comparative FT-IR spectra of conventional and 9-VT-SE-PSPTC (Note: Since absorbance is the direct measure of the concentration of respective functional stretching, it has been calculated from transmittance mode to absorbance mode by measuring I_0(Incident radiation) and I (Transmittance radiation) by drawing a straight line tangent to the C–Cl and C–N stretching, $A = \log(I_0/I)$).

The SEM and EDAX analyses were carried out one by one for each loaded sample and hence, the sample preparation for both techniques were the same for both group I and II, catalysts. Since all the synthesized catalysts are non-conducting polymeric materials, and in order to analyze through SEM and EDAX, it is essential to make them as conducting materials by a gold coating technique. The best methodology to prepare the sample was by

Table 2. Quantitative FT-IR absorbance results of characteristic peaks for first and second group 0 VT's and SE-PSPTCs.

Name of the catalysts	Group I catalysts			Group II catalysts		
	Absorbance of C–Cl stretching (710 cm^{-1})	Absorbance of C–N stretching (1158 cm^{-1})	Absorbance ratio of C–Cl/C–N	Absorbance of C–Cl stretching (710 cm^{-1})	Absorbance of C–N stretching (1158 cm^{-1})	Absorbance ratio of C–Cl/C–N
0VT	0.52	0.08	6.50	0.47	0.06	7.83
3VT	0.41	0.17	2.41	0.40	0.13	3.07
6VT	0.27	0.33	0.81	0.29	0.25	1.16
9VT	0.11	0.51	0.21	0.17	0.39	0.43
12VT	0.09	0.54	0.16	0.16	0.42	0.38
15VT	0.08	0.60	0.13	0.15	0.45	0.33

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taking common mesh size ($-120 + 140$) beads from different types of both groups and spread them onto a surface of the double-side adhesive tape in which one side was adhesived on the surface of circle-shaped copper disc pivoted by a rod. The adhesive bead catalyst on the surface of the copper disc has not been compressed forcefully or compacted in order to retain the original morphology of the catalysts without changing. The JEOL fine coat ion sputter JFC1100 was used to give the gold coating of all the catalysts under identical experimental condition and thickness of the gold coatings was maintained at about 40 Å for both groups of samples. Then, these gold coated samples were subjected to analyses of SEM and EDAX. Since we were applying EDAX analysis as a quantitative measurements of surface chloride, adequate care has been taken for preparing the sample and also the experimental parameters were kept constant.

As already mentioned, the SEM viewed samples were simultaneously subjected to EDAX analyses. The operating signal was kept at 25 keV and detection depth limits for all the samples were maintained in the range of 0.5μ to 1μ. Because of a identical gold coating on the surface of different types of each group catalysts, the gold deposited on the surface is constant for all the catalysts and hence, irrespective of all types and groups of catalysts, the peak area of Au was constant, only the peak area of Cl may be varied based on its surface enrichment of chloride with respect to PPT. For comparative purpose, the amount of Au and Cl was accounted through inbuilt software of the instrument and was executed as both the normalized EDAX spectrum and its corresponding Au, Cl percentage keeping Au quantity as base.

The specimen for ESCA analyses were prepared by taking a common mesh size ($-120 + 140$) of unquaternized polymer beads from each group and was spread on the Indium foil and was fixed on it by mild pressing and baked for 1 h at 60°C before loading in the analysis chamber. Since we were comparing the amount of surface bound benzyl chloride ($-CH_2Cl$) for each group, the data collecting parameters of the instruments were also kept the same for all the samples. Furthermore, detection depth information limit was maintained in the range of $20-30$ Å and the instrument resolution was 0.8 eV. During analysis, the base pressure of the chamber was kept at 8×10^{10} mbar. Al ka (1486.6 eV) was used as the exciting source and a pass energy of 100 eV and 20 eV were used for data collection. The system binding energy was standardized by Au $4f_{7/2}$ line which was observed at 83.3 eV. In order to ascertain the superiority of the SE-PSPTC from each group, the amount of covalent surface chloride(Cl) and surface carbon(C) were quantitatively estimated using a suitable software, viz, "eclipse." The estimated percentage of surface carbon and surface chloride for I and II group of catalysts are given in Table 4.

Kinetic Experiments for Various Addition Reaction to Olefins

The catalyzing efficiency of the individual catalysts from each group was ascertained by studying the dichlorocarbene addition reaction to different olefines viz. 1-octene, styrene, cis-cyclooctene and cyclohexene. The reaction was carried out under pseudo first-order kinetics. Since we are examining the efficiency of all the catalysts (I and II) for comparison study, the reaction conditions were maintained identically for all types of both groups by taking a common mesh size (i.e., $-120 + 140$) as the catalyst. A 150 ml

threeneck round bottomed flask fitted with a double walled condenser and mechanical stirrer with a 45×18 mm curved teflon blade was placed in thermostatic water bath having the temperature fixed to $30 \pm 0.2°C$. Then, the flask was charged with 0.2 g of respective conventional and SE-PSPTC's, 45 ml of (30% w/w) NaOH and 12.75 mmol of respective olefines and stirred at 100 rpm for 5 min to condition the catalyst and then stirring speed was increased to 600 rpm and 40 ml of chloroform was added at zero time. After every 5 min interval, the organic samples were withdrawn from the flask and was subjected to GC analysis. The disappearance of respective olefines was followed to determine the rate constants. The pseudo first order rate constants were evaluated from the plots of $\log(a - x)$ vs. time. By maintaining the same reaction condition, each olefine with definite mole concentration (12.75 mmoles) was individually studied.

RESULTS AND DISCUSSION

In the bead shaped PSPTC, if the active site is available inside the beads, it may not be available for reaction, particularly for those substrates having a bulky/complicated structure. As a result, about 50% of active site functionalities are influxed inside the supporting monomers network and become waste.[35,38] It is also known that during the preparation of the bead catalyst, if hydrophilic functional monomers are used in the preparation of copolymer beads by suspension polymerization, the functional group (catalytic site) may reach the surface of the beads due to hydrophilic interaction. Though this strategy is good for surface-enrichment of the active site, the need for chemical inertness severely limits the use of polymers which contain hydrolysable groups, active OH or NH group or groups that can be easily oxidized or reduced.[39] Polymers with such functional groups include poly(acrylates), polyesters, poly(acrylamides), polyamides (e.g. nylons and peptides), polyurethanes and polysaccharides. In view of this, it is not surprising that polystyrene and their related functional monomer, like VBC/VT, is the most commonly used support or active site in the preparation of polymer bead-catalyst. Furthermore, right from the initial period of PSPTC, because of a reactive chloromethyl group in VBC, it has traditionally been used as a precursor for functionalization. It is always worthwhile to consider the cost factor for any catalyst preparation. In this connection, it is to be pointed out that VBC used for the preparation of PSPTC is costlier than VT.

Although there were a number of studies on the preparation of microporous bead-shaped insoluble polymer-supported catalysts in the literature, there is absolutely no report on the bead-shaped catalyst containing all the active sites on the surface. In particular, the study of surface-enriched with active site polymer-supported phase-transfer catalyst by a suspension polymerization technique, using other than VBC as functionality,[35] has not appeared anywhere in the literature. However, we firmly suspect that the conventional methods reported by Balakrishnan et al.[12] and Mohanraj et al.[34] for the preparation of insoluble PSPTC beads using vinylbenzylchloride and vinyltoluene, respectively as functional monomers may lead to the possibility of this expensive functionality buried inside the poly(St/DVB) network and also they render diffusional limitations into and out of the polymer matrix during chemical reactions. In both reports, the addition of a functional monomer (VBC and VT, respectively) was next to the supporting monomers

St/DVB, and that leads to the functional groups embedded inside the poly(St/DVB) network and becomes waste. Particularly in Mohanraj's et al.[34] method, although it suggests replacement of costly functionality viz., VBC to inexpensive functionality VT for the preparation of PSPTC, the preparation methodology again leads to wastage of VT by buried functionality inside the poly(St/DVB) network due to the simultaneous addition of VT to supporting monomers (St/DVB). Further, it is better to concentrate the synthesis function in such a way that all the active sites are on the surface of the beads. Unfortunately, the existing conventional methods reported in the literature[34] are not suitable to bring the active site to the surface of the beads. In addition, this technique has not provided any guarantee about the maximum utilization of -CH_2Cl (active site region) for the catalytic process.

Hence, our objective was to prepare the PSPTC using inexpensive vinyltoluene as a functionality by modifying the experimental strategy followed by the Mohanraj et al.[34] and Balakrishnan et.al.[12] methods. Using the optimized procedure for the synthesis of a novel surface-enriched polymer-supported phase transfer catalysts, we prepared two groups of catalysts by varying the crosslinking ratio as 2% and 6%, respectively and fixing the 25% of active site monomer (VT) as common. Each group contains 6 different types of beads by varying the PPT of St/DVB. These two groups have been prepared with the purpose of learning the extent of surface-grafting at higher crosslinking ratios. When we use VT as a functional monomer, first the functional methyl (—CH_3) has to be chlorinated and then converted into a catalyst. Unless the methyl groups are available on the surface, the process of effective chlorination and then quaternization will be difficult. Ultimately, there may be a reduction of the catalytic site, 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. Hence, in this study we report the complete picture regarding the entire PPT process and how an optimum PPT period can be useful to bring maximum poly(VT) on the surface of poly(St/DVB) and their evidence and effects on chemical reactions.

Evidence for the Surface Grafted Poly(VT) on Poly(St/DVB) Copolymer Beads

In both groups during the preparation of copolymer beads, the functional monomer viz. VT was added after the partial polymerization time 3, 6, 9, 12, and 15 h. The important questions that arise are: (1) whether the functional monomer has homopolymerized (due to the availability of the free radicals from AIBN), especially at higher PPT and due to the non-availability of living radicals of poly(St/DVB) and, (2) whether poly(VT) has chemically grafted on poly(St/DVB) or physically adsorbed on the surface of the beads. This has been cross-examined by the precipitation technique. The mother liquor, i.e., the solution obtained after filtration of the polymer beads was subjected to a precipitation process with an excess of non-solvent (methanol) for poly(VT).There was no precipitate obtained from the mother liquor of different types of PPT yielded filtrate solutions in both groups. The absence of a precipitate confirms the absence of homopolymerization of VT monomer. It is also confirmed that because of a constant stirring (400 rpm), coupled with a

long polymerization time, and at suitable polymerization condition, all the monomers were polymerized and converted to terpolymer beads.

Furthermore, to clarify the second doubt i.e., the chemical bonding or physical adsorption of poly(VT)on poly(St/DVB), swelling experiments were carried out using 2 g of dried copolymer beads ($-120 +140$ mesh size) of each group with each type using 75 ml of toluene, an excellent solvent for poly(St/DVB). This was stirred continuously using a magnetic stirrer for 3 days at room temperature at optimum speed. Then, the resulting toluene extract was poured into an excess of methanol for the precipitation of any adsorbed polymer (i.e., poly(VT) on poly(St/DVB) beads in the respective group. Here also, no precipitate for any type in each group was obtained proving that poly(VT) is chemically grafted on the surface of poly(St/DVB). Therefore, the possibility of physical adsorption of VT or poly(VT) over poly(St/DVB) has been logically ignored. Further, the delayed introduction of functional monomer viz., VT may be an appropriate technique to bring most of the $-CH_3/-CH_2Cl$ groups on the surface of the beads.

Estimation of Total [Cl⁻] in Conventional and SE-PSPTC'S and Their Corresponding Inferences

The first and second group beads obtained from different PPT's were enriched with $-CH_3/-CH_2Cl$ groups on the surface, and therefore they easily undergo quaternization compared to conventional beads. The estimated total free chloride ion concentration for both the groups (Table 1) of a representative mesh size were gradually increased from a conventional catalyst (0 VT) to 9 VT-SE-PSPTC. Obviously, the extent of quaternization has varied based on PPTs. In both groups, irrespective of mesh size, the chloride ion concentration gradually increased from 0 VT to 9 VT and then 12 VT and 15 VT were similar to that of 9 VT without much of an appreciable increase. This is because, when the PPT of St/DVB increased from 3 h to 9 h, the grafting of VT on poly(St/DVB) would increase. That is, when the PPT is 3 h, the amount of St/DVB in the monomer form was more and on introduction of VT, a fraction of it may have homogeneously mixed with St/DVB droplets, and there is a possibility of this, (VT) buried more inside the poly(St/DVB) beads. However, when PPT is increased, the copolymerization of St/DVB also increased and the availability of the free monomer i.e., St and DVB is less and so the introduction of a functional monomer may more often than not get grafted on the surface without getting inside the polymer network of poly(St/DVB) as the PPT is raised from 3 to 9 h. The 12 and 15 h PPT does not influence the grafting efficiency of poly(VT) on poly(St/DVB) and becomes saturated.

In the conventional method, polymer beads were prepared by a homogeneous mixing of this functional monomer VT, along with supporting monomers poly(St/DVB) without allowing partial polymerization time (i.e., PPT = 0), the VT may be uniformly distributed inside the poly(St/DVB) network and there is less of a chance on the surface of the beads. The same results are also obtained for the second group of beads. The increasing of crosslinking ratio from 2 to 6% does not greatly influence either the reduction/increasing of grafting of poly(VT) over the poly(St/DVB) network. Therefore, the facile quaternization has been possible if most of the $-CH_2Cl$ groups are available on the

surface so that the chlorinating agent (SO$_2$Cl$_2$) and quaternizing agent (triethylamine) could easily react with —CH$_3$/—CH$_2$Cl without diffusional difficulties.

Hence, the increasing trend of chloride ion concentration from 0 VT to 9 VT confirms the availability of more —CH$_3$/—CH$_2$Cl groups on the surface. It may be inferred that grafting of poly(VT) on poly(St/DVB) had further increased with an increase in PPT. The constant [chloride ion] after 9 PPT implies that the surface-grafting of poly(VT) is saturated, hence, further allowing PPT of St/DVB to 12 and 15 h does not leads to further grafting. Hence, PPT of 9 h may probably be an optimum period for better surface grafting. In addition, the overall [chloride ion] between the first and second groups, irrespective of PPTs and different mesh size, does not alter much. That is, the [chloride ion] of the first group catalyst is almost the same for different PPTs of the second groups, even though the crosslinking was increased from 2 to 6%, this inference ignores the early studies[15,40] viz. increase in percentage crosslinking has remarkably decreased the [chloride ion] and the observed rate constant. In both groups, the [chloride ion] of 9 VT has increased twice, when compared with conventional (0 VT) catalysts which strongly supports the availability of —CH$_3$/—CH$_2$Cl group on the surface irrespective of the percentage of crosslinking.

Determination of Surface [Cl] and [Cl$^-$] Based on Various Surface-Characterization Techniques

The estimation of [chloride ion] analysis through a titrimetric method for all the catalyst is the sum of the [Cl$^-$] both inside and on the surface of the beads. To confirm the surface chloride (covalent/ionic) of the beads, we have employed the other sensitive surface characterization techniques viz. FT-IR, SEM, EDAX, and ESCA.

Fourier transform-infrared spectroscopy is the most widely used method among the techniques available for the characterization of crosslinked[41,42] resins and polymer supported catalysts.[43,44] Employing FT-IR as a quantitative technique has rarely been discussed in the field of PSPTC's. Since these catalysts contain sensitive functional groups, we have used this technique to assess the surface-enrichment of an active site in the different SE-PSPTC of each group by a semi-empirical method. It is known that the efficiency of the catalyst depends upon the degree of conversion of pendant benzyl chloride group (—CH$_2$Cl) into an active site (—CH$_2$N$^+$(C$_2$H5)$_3$ Cl$^-$) group. There again, the extent of quaternization depends on the position of the —CH$_2$Cl group (i.e., either on the surface or inside the polymer beads). The decrease/disappearance of a characteristic peak intensity of C–Cl stretching (710 cm^{-1})[45,46] and the corresponding increase in the peak intensity of C–N stretching (1158 cm^{-1})[46,47] favors the formation of a catalytic site of the catalysts. The transmittance values of the C–Cl and C–N peak intensity has been converted to absorbance by measuring the I$_o$ and I height through the baseline method that leads to A = log(I$_o$/I) for the first and second group catalysts (Table 2). The absorbance values reveals that C–Cl has gradually decreased from 0 VT (Fig. 1a) to 9 VT (Fig. 1b) and then remains almost constant in 12 VT and 15 VT. In the case of C–N stretching, the absorbance value is gradually increased from 0 VT to 9 VT, and then remains almost constant. Similarly, the C–Cl/C–N ratio also consistently decreases and remains almost constant. This may be attributed to more grafting of poly(VT) from 0 VT to 9 VT in both

groups, irrespective of the percentage of crosslinking. The constant absorbance value of 12 VT and 15 VT implies that a further increase of PPT does not enhance grafting significantly. This lends support for the higher active site in 9 VT SE-PSPTC (at lower PPT), because more quaternization (C–N stretching) has been possible if most of the $-CH_3$ groups are available on the surface, which in turn increases the facile chlorination($-CH_2Cl$) and quaternization(($-CH_2Q^+Cl^-$) without any diffusional limitation.

The poly(VT) grafted first and second group SE-PSPTCs and their corresponding conventional catalysts were viewed and assessed through a scanning electron microscope. The surface morphology of the first group conventional catalyst (Fig. 2 a,b) and the second batch conventional catalyst that is 0 VT has a relatively neat smooth surface. Whereas, different PPT based SE-PSPTCs of both groups were found to have a rough surface and the formation of a nodules-enriched surface is favored with increasing the order of PPT for St/DVB. The concentration of surface-grafted poly(VT) nodules are found more in 9 VT of the first (Fig. 3 a,b) and second group catalysts compared to the rest of the catalysts of lower PPTs. But, 12 VT and 15 VT in both batches had an almost similar morphology like 9 VTs. The surface grafted nodules must be the result of chemical grafting of poly(VT) on the particles of poly(St/DVB). The smooth surface in conventional catalysts (0 VT) of both groups may be due to a concomitant mixing of all three monomers leading to a uniform distribution of the functional monomer (VT) inside the beads of the poly(St/DVB) net work, irrespective of their crosslinking. Furthermore, VT and DVB are more reactive than styrene and when all the monomers are mixed together, homogeneous terpolymer beads have been positively formed. But, in the case of rough/nodules, the enriched surface in SE-PSPTCs may due to prepolymerization of supporting monomers (St/DVB), and also a delayed introduction of functional monomers (VT) lead to grafting on the surface of poly(St/DVB), and thereby enriched the surface with nodules of poly(VT) based on PPT of St/DVB. The increasing trend of grafted poly(VT) nodules on the surface with respect to increasing the partial polymerization time of St/DVB is because, during more PPT, most
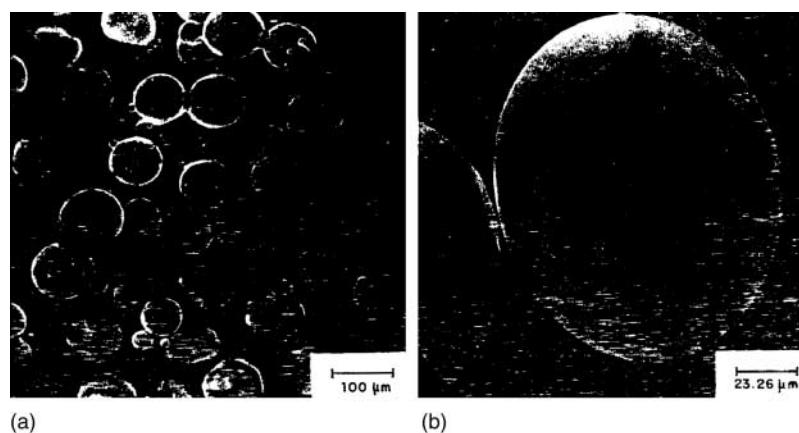
Figure 2. SEM image of first group conventional catalyst (0 VT) (a) Overall view; (b) Magnified single bead view (0 VT).
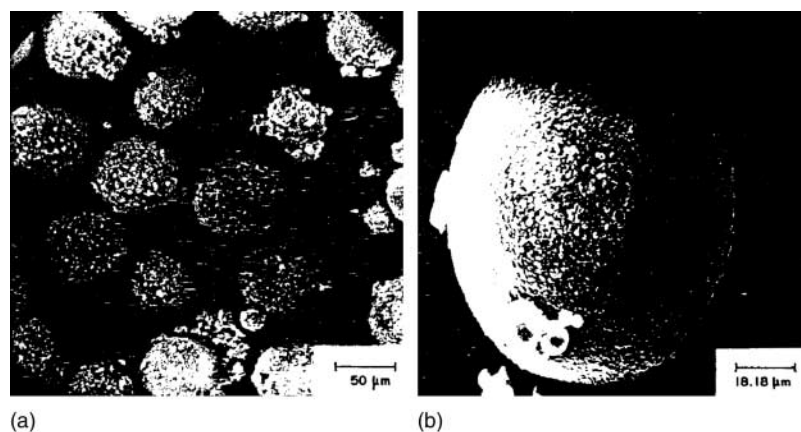
Figure 3.   SEM images of first group 9-VT-SE-PSPTC (a) Overall view; (b) Magnified single bead view.

of the St/DVB monomer has been formed as the primary poly(St/DVB) network. Also, the delayed introduction of VT molecules have to chemically get grafted on the surface only. This subsequently increases the surface enrichment with a ($-CH_2Cl$) group, which in turn gets quaternized and appears as nodules in the SEM images. The high concentration of nodules/rough surface at 9-VT-SEPSPTCs must be the result of surface grafting of poly(VT) and also explains that 9 h is the maximum/optimum PPT period to bring most of the poly(VT) nodules on the surface in both groups. Similarly, 12 VT and 15 VT has also exhibited the same surface morphology like 9 VT for both groups. But, allowing PPT more than 9 h, in no way enhances the grafting of VT on the surface and therefore, higher PPT is logically ignored. Ruckenstein et al.[48] and Su Chou et al.[49] also reported a similar surface morphology in their studies.

The calculated percentages of chloride and Au for the first and second group catalysts (Table 3) reveals that, in both groups, the chloride percentage continuously increases up to 9 VT, then remains almost constant for 12 VTs and 15 VTs. Obviously, the percentage of Au is decreasing up to 9 VT and remains constant. The amount of Au was maintained as constant (under identical gold coating) and it was treated as 100%, and thereby either increasing or decreasing the percentage of Au certainly depends upon the amount of surface chloride of the individual catalysts. The constant increasing of the Cl percentage from 0 VT to 9 VT, irrespective of the amount of crosslinking of the first and second groups, proves the consistent enrichment of the active site on the surface with increasing PPT of the St/DVB. The insignificant changes in the Cl percentage for 12 VTs and 15 VTs indicates the saturation of poly(VT) grafting on poly(St/DVB). The normalized EDAX spectra of the first group conventional catalysts (Fig. 4a) and their corresponding notable 9 VT catalysts spectra (Fig. 4b) are shown as proof of the above observation. It is very clear from the above inference that in both groups, 9 VT has good SE-PSPTC due to its higher percentage of Cl compared with lower PPTs catalysts. The studies of Hong et al.,[45] Ruckenstein et al.,[48] and Jabbari et al.[50] support the utilization of EDAX to study the assessment of surface-chloride of PSPTC based on the peak intensity of chloride.

Table 3. EDAX semi-quantitative analysis data of gold and chloride for first and second group 0 VT's and SE-PSPTC's.

Name of the catalysts	Group I catalysts		Group II catalysts	
	Atomic % of gold (Au)	Atomic % of chloride (Cl)	Atomic % of gold (Au)	Atomic % of chloride (Cl)
0VT	88.91	11.09	90.88	9.12
3VT	77.19	22.81	79.86	20.14
6VT	49.03	50.97	52.36	47.64
9VT	22.33	77.67	26.32	73.78
12VT	19.96	80.04	23.77	76.23
15VT	17.86	82.14	20.97	79.03

Yet another surface study viz. ESCA is one of the powerful techniques to determine the surface elements, either quantitatively or qualitatively, in the samples.[51–53] The unquaternized copolymer beads obtained from different PPTs of both groups and their corresponding conventional 0 VTs beads were taken for analysis with a view aimed at learning about the enrichment of the $-CH_2Cl$ group on the surface. Since these copolymer beads were prepared from VT, St, and DVB and hence, its chemical constituent must be composed of carbon (C), hydrogen and chloride (Cl). The line position from Al X-rays are positioned as follows: C 1S 287 eV, Cl $2P_{3/2}$ 199.91 eV, Cl $2P_{1/2}$ 201.5 eV.[54,55] The overall survey scan of ESCA for the first (Fig. 5) and second group conventional-0 VT and 9 VT beads sample reveals that the elements such as carbon, chloride, indium, and oxygen are present on the surface of the beads. The XPS peak relating to C 1S at 287 eV is in good agreement with the literature findings.[54,56] Similarly, the characteristic covalent chloride
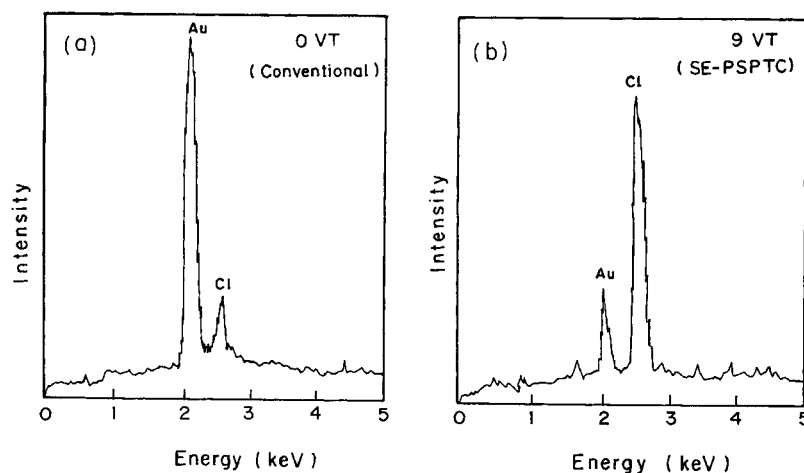

Figure 4. Comparative EDAX spectra of first group catalysts (a). Normalized EDAX spectra of conventional catalyst (0 VT); (b). Normalized EDAX spectra of 9-VT-SE-PSPTC.
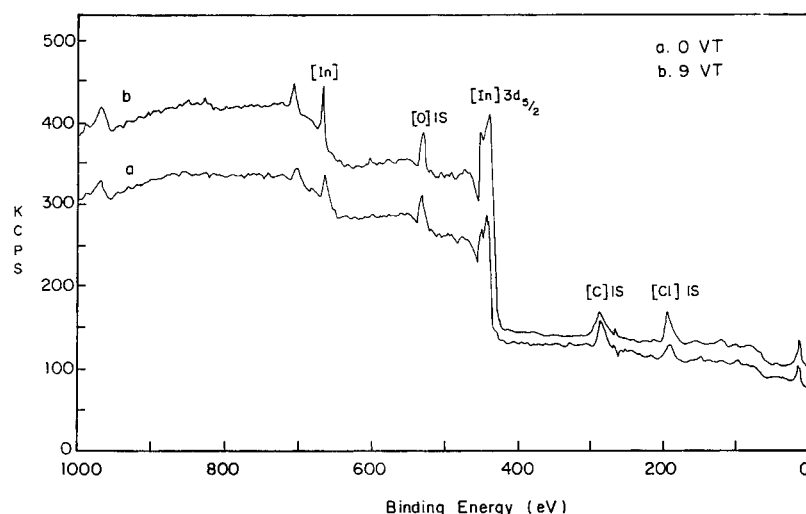
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Figure 5. Comparative ESCA survey spectra of first group unquaternized 0 VT and 9 VT polymer beads.

(active site response) is observed with the binding energy value of 199 eV which also coincides with the literature value. In the same manner, the survey spectrum of both groups of different PPTs beads were also observed within the same BE values of their respective elements.

In order to ascertain the surface elements quantitatively, particularly carbon and chloride, the contents are calculated using "Eclipse software." Table 4 contains the calculated results in terms of percentage of carbon and chloride from the software using all the catalysts and the rest of the percentages were a contribution of indium and oxygen. From the values in Table, it may be observed that in both groups, the percentage of surface chloride increases from 0 VT to 9 VT and 12 VT and 15 VT have almost similar percentages to those of 9 VT. But, in contrast, the surface carbon gradually decreases from

Table 4. ESCA surface analysis results of carbon and chloride for first and second group 0 VT's and SE- PSPTCs (quantitative).

Name of the catalysts	Group I catalysts		Group II catalysts	
	Percentage of chloride	Percentage of carbon	Percentage of chloride	Percentage of carbon
0VT	11	55	10	57
3VT	17	49	16	52
6VT	20	43	19	47
9VT	24	39	23	41
12VT	25	36	24	38
15VT	26	32	25	35

0 VT to 9 VT and remains almost constant thereafter. This opposite trend of increasing percentages of Cl with decreasing percentages of carbon with increasing PPT of St/DVB would explain the following inference. In 0 VT, all three monomers (i.e., St, DVB, and VT) were homogeneously mixed together and thereby the surface carbon of 0 VT must be the contribution of the carbons of all three monomers. Hence, the percentage of carbon increases, whereas the percentage of chloride is less on the surface. On the other hand, when partial polymerization of St/DVB is carried out from lower PPT to higher PPT, most of St/DVB has been formed as beads, and a delayed introduction of VT leads to grafting on the surface and therefore, the outer layer of the beads contain the carbon of VT molecules alone. Since St/DVB carbons are available inside the layer, the percentage of carbon decreases and subsequently increases the surface chloride amount proportional to their PPTs. The twofold increase of the chloride percentage in both the group of 9 VT, compared to their 0 VT, would strongly support the enrichment of the active site on the surface. The constant chloride percentage for 12 VT and 15 VT of the respective crosslinking proves the saturation of grafting at 9 h PPT. A similar type of study of chloride on the triphase catalyst was also reported by Hong et al.[45] and Su-Chou et al.[49]

Assessment of Catalytic Efficient Through Chemical Reaction

Apart from the [chloride] and various surface characterization analyses, assessment of catalytic activity of different catalysts were also ascertained by studying different olefines addition reactions. Although, different surface analyses results support the enrichment of an active site on the surface on increasing PPT of St/DVB, but when those catalysts were employed in a chemical reaction, their catalytic effect may vary due to the reaction conditions and physical behavior of the catalyst. Hence, to confirm the superiority of the catalyst in the reaction medium, the rate constants were determined using four different olefins. The values (Table 5) explain that irrespective of olefine, the rate constants are found to increase from 0 VT to 9 VT-SEPSPTC and remains constant for 12 VT and 15 VT SE-PSPTC in both groups. Generally, a higher rate constant is possible when most of the active sites are located on the surface so that the substrate molecules can easily interact with active sites in a shorter contact time without any diffusional limitation and, which in turn, increase the rate constant. The increase in rate constant from 0 VT to 9 VT SE-PSPTC confirms the enrichment of active sites proportionally with PPT of St/DVB. The similar rate constant for 12 VT and 15 VT SE-PSPTC's ensures the saturation of surface grafting of VT. On comparison of the rate constant for 0 VT and 9 VT in each group, it is observed that 9 VT has a two-fold increase, even though the same amount of functional monomer (VT) was employed for preparation of the catalysts. This trend concretely supports the fact that at least half the amount of the functional monomer (VT) was not utilized for a reaction purpose in the conventional catalyst (0 VT).

As observed in the various surface characterization technique results, this is due to the concomitant mixing of all three monomers, which ends up in 50% of the amount of VT molecules buried inside the poly(St/DVB), and this may not be available for the reaction purpose particularly with reference to bulky substrate reactions. On the contrary, the delayed addition of a functional monomer seems to bring almost all the active sites on the surface, particularly during the 9 PPT technique. Hence, 9 VT is the best SE-PSPTC

Table 5. Comparative rate constants of different olefins addition reactions.

| Name of the catalyst | Rate constant of group I catalysts $k_{obs} \times 10^3 \sec^{-1}$ | | | | Rate constant of group II catalysts $k_{obs} \times 10^3 \sec^{-1}$ | | | |
| | Substrates | | | | Substrates | | | |
	1-Octene	Styrene	Cis-cyclo octene	Cyclohexene	1-Octene	Styrene	Cis-cyclo octane	Cyclo hexene
0 VT	3.9	2.5	1.9	1.4	3.3	2.1	1.1	8.8×10^{-4}
3 VT	4.5	3.3	2.3	1.9	3.9	2.8	1.4	1.1
6 VT	5.2	3.8	3.1	2.3	4.6	3.3	1.8	1.3
9 VT	6.3	5.2	4.0	2.8	5.3	4.4	3.2	1.8
12 VT	6.5	5.5	4.2	2.9	5.5	4.7	3.6	2.0
15 VT	6.6	5.6	4.2	3.0	5.7	4.8	3.7	2.0
Recovered (9 VT)	5.4	4.3	3.4	2.1	4.6	3.6	2.8	1.2
Regenerated (9 VT)	6.2	5.0	3.9	2.8	5.0	4.2	3.2	1.6

catalyst than the rest in both groups, irrespective of the percentage of crosslinking. Furthermore, the stability of the catalysts was also examined by reusing the recovered catalyst (9 VT-re) and regenerated catalyst (9 VT-rg) in the same reaction. The isolated catalyst from the reaction mixture was dried and regenerated in the original Cl$^-$ from treatment with 3 N HCl/THF by simple shaking with a sufficient time of anion exchange, then washed with THF/distilled water and dried. The recovered (second cycle) catalyst had shown almost a 5 to 9% decrease in the rate constant compared to the original catalyst (Table 5), whereas the regenerated catalyst had shown only a negligible decrease in rate constant compared to the original catalyst. This would support the stability of the active site grafted on surface. Furthermore, the higher crosslinking ratio (2 to 6%) has not affected the rate constants of the reactions. Therefore, this surface-grafting method is proved to be a good method as it paved the way to bring all the active sites on the surface.

CONCLUSION

The conventional bead-shaped (0 VT) PSPTC preparation method involves the addition of functional monomer (VT) along with supporting monomers, and that process leads to most of the active site inside the polymer network becoming inaccessible for reaction. To avoid this disadvantage and to bring the active site influxed to the surface of the bead, we successfully prepared a surface-enriched polymer-supported phase-transfer catalyst (SE-PSPTC) by following the delayed addition/surface-grafting strategy of the functional monomer over the prepolymerized surface of the poly(St/DVB) network. To examine the degree of surface-grafting of poly(VT) on the surface, we prepared two groups each containing six different types of SE-PSPTC by varying the crosslinking ratio from 2% to 6%, respectively and different PPTs of St/DVB. The experimental results

obtained from various surface analyses and also a chemical reactions method shows that there is an increasing trend of [chloride ion] by the Volhard method, [C–N stretching absorbance] by FT-IR, larger poly(VT) nodules concentration on the surface of the beads through SEM, higher % of surface chloride via EDAX, the increasing/decreasing trend of surface covalent chloride/carbon and higher rate constants irrespective that olefins are lying on par with the partial polymerization time of St/DVB. This observation conclusively proves the gradual surface-enrichment of the active site from 0 VT to 9 VT-SE-PSPTC and remains constant at 12 and 15-SE-PSPTC catalysts. Although, we had added the same amount of functional monomer starting from the conventional (0 VT) to the other SE-PSPTCs, we find, that in all the above analyses, there is a two-fold enhancement of surface chloride between 0 VT and 9 VT-SE-PSPTCs, irrespective of the groups. This would strongly suggest that we have successfully brought the active site on the surface $\simeq 50\%$ by following a delayed addition strategy of the functional monomer from a conventional preparation method. Therefore, 9 VT-SE-PSPTC having least PPT and also vast active sites on the surface, 12 and 15 PPT SE-PSPTC for 2 and 6% crosslinking does not influence the degree of surface-enrichment of active sites much. As a result of this study, it is proved that in bead-shaped polymer-supported phase-transfer catalysts, if active sites are located on the surface, the catalytic efficiency increases, and also enables us to perform effectively reactions involving bulky substrates which is difficult in conventional catalysts due to the diffusional limitations of the substrates.

ACKNOWLEDGMENT

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