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Onium Chains–Silica as Catalytic Support: Application to Hydroformylation

L. HONG AND E. RUCKENSTEIN[1]

Department of Chemical Engineering, State University of New York at Buffalo, Box 60, Buffalo, New York 14260-4200

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Polymer chains of quaternary oniums are deposited on the surface of hydrophilic silica by the radical polymerization of water-soluble quaternary onium monomers present in a water medium which imbibes the porous silica. The modified (quaternized) silica surface which contains a small amount of water is a more suitable support than silica, since it provides anchors for the catalytic species and sites for the adsorption of reactant molecules. It is used as substrate for the immobilization of monosulfonated triphenylphosphine (DPM) and of its rhodium carbonyl complex $Cl(CO)Rh(DPM)_2$, through an ion-exchange process. The immobilized catalytic system containing a small amount of water was employed in the hydroformylation of styrene and ethyl 10-undecenoate. The presence of ethanol in the reaction medium is necessary to achieve a high yield of aldehydes. For styrene, the ratio of the isomer to the normal aldehyde is greater than 6, while for ethyl 10-undecenoate, it is $\frac{1}{4}$. Structural factors that affect the regioselectivities of the aldehydes are suggested as possible explanations for the above ratios. The performance of the catalyst has remained almost unchanged during several reuses.

INTRODUCTION

The use of very expensive complexes as homogeneous catalysts (usually they contain noble metal ions or chiral ligands) generated the problem of catalyst recovery. A number of techniques of heterogenization of the homogeneous catalysts have been therefore developed (*1*). Among them the use of water-soluble complexes in water–oil biphase catalytic systems represents an important development (*2*), which offers the following advantages over other immobilization procedures: (1) one can bind water-soluble groups such as carboxyl, sulfonate, or onium salts to various ligands (*3*); (2) the catalyst and the reaction products can be separated by phase-separation; (3) the reactivities and selectivities can be controlled by modifying the structure of the water–oil interface with surfactants, polymers, or polymerized surfactants (*4*); and (4) the catalyst often exhibits higher stability under high pressure of carbon monooxide in carbonylation reactions (*5*). The sulfonated phenylphosphines (*6*) have been frequently used as water-soluble ligands, and the transition-metal complexes thus obtained have been used to catalyze the hydroformylation (*6*), the alkylation (*7*), the hydrogenation (*8*), the ring-opening metathesis polymerization (*9*) reactions, and the photochemical reduction of water (*10*).

The hydroformylation reaction (oxo reaction) of an olefin with syn-gas (H_2/CO) to obtain an aldehyde with one additional carbon, is of industrial importance in the synthesis of a number of fine organic compounds (*11*). The technology of using sulfonated phosphine–rhodium carbonyl catalysts for the hydroformylation of propene, developed by Rhône–Poulenc and Ruhrchemie (*12*), has solved in a satisfactory manner the problem of reusing this extremely expensive catalyst which is highly active and selective under mild reaction

[1] To whom correspondence should be addressed.

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conditions. Although this development has potential significance in the oxo reaction of higher molecular weight olefins, including olefins with functional groups, in water–oil biphase systems, the accessibility of the nonvolatile olefin molecules, that are usually dissolved in an organic solvent, to the water-soluble catalyst is always very low. For improving this shortcoming, alkyl substituents have been bound to the sulfonated phenylphosphine ligands to increase their surface activity (*12*), or a small amount of a polar organic solvent, such as ethyl acetate, ethanol, or acetone, was added to the two-phase system to generate a border layer with a suitable polarity able to mediate the contact between the catalyst and the reactant. These methods increase, however, the risk of losing rhodium species to the organic phase. One of the best solutions seems to be offered by the combination of high-performance ultrafiltration membranes of aromatic copolyamides with the catalyst; it resulted in a highly efficient recovery of rhodium complexes (*13*), but represents a more complicated technology.

Recently, an interesting innovation based on the adsorption of the water-soluble complex $HRh(CO)(TPPTS)_2$ {where TPPTS is triphenylphosphine trisulfonate $P(m\text{-}C_6H_4SO_3Na)_3$} and of a small amount of water on a high-surface-area hydrophilic support (silica or porous glass) was suggested by Davis (*14*). In this procedure, the hydrophilicities of the ligand TPPTS and of the support generate sufficiently large interaction energies to ensure the stability of the immobilization. The water content of the catalyst greatly influences its performance, the optimum water-content being 8.5 wt%. When the water content was increased to 45 wt%, the yield of the aldehyde fell to less than 10% of its optimum value (*15*). This probably happens because as the water content increases the immobilized catalyst becomes increasingly segregated from the hydrophobic olefin molecules. It is, however, not easy to uniformly coat a high-surface-area support with small amounts of water, particularly in large-scale processes.

In this paper, we suggest another method for the immobilization of the water-soluble sulfonated phenylphosphine rhodium–carbonyl complexes to a silica support. The sulfonated triphenylphosphine $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (denoted DPM) is attached to a silica surface on which poly(vinylbenzyl triethylammonium chloride) {P(VEAC)} was previously deposited. The quaternization of the silica surface was carried out by immersing the porous silica into an aqueous solution of VEAC containing the initiator $K_2S_2O_8$, followed by the evaporation of most of the water. The solid containing about 60 wt% water thus obtained was introduced into a high boiling hydrocarbon medium for polymerization. The catalytic species were bound to the quaternized surface by immersing the functionalized silica powder in an aqueous solution containing the rhodium complex $Cl(CO)Rh(DPM)_2$ and the ligand DPM.

The presence of the quaternary onium groups on the water containing surface increases the compatibility between the water and oil phases, thus facilitating the contact between the olefin molecules and the catalytic sites. The performance of the present catalyst was found to be enhanced when ethanol was introduced into the system. For example, when ethyl 10-undecenoate was hydroformylated, the yield of the aldehydes increased about five-fold as the volume fraction of ethanol was increased from 1.2 to 11% in the mixture of ethanol and cyclohexane. This occurs probably because the polymer chains containing pendant ion-pairs are swellable by ethanol molecules, and this increases the flexibility and hence the accessibility of the catalytic polymeric chains.

In the present paper, both styrene and ethyl 10-undecenoate were used for hydroformylation at 85°C and 750 psi (CO/H_2 = 1); the molar ratio of the phosphine ligand to rhodium was 10, and of the olefins to the rhodium complex about 4000 for styrene and 2400 for ethyl 10-undecenoate. We observed

that when the hydroformylation of styrene was carried out for 15 h, 56% of styrene was converted to aldehydes, with a ratio of 2-phenylpropanal to 3-phenylpropanal greater than 6. The latter feature is important in the synthesis of 2-(*p*-isobutylphenyl) propanal from *p*-isobutylstyrene; the subsequent oxidation of this aldehyde generates ibuprofen, an over-the-counter analgesic (*16*). The aliphatic compound ethyl ester of 10-undecylenoic acid, which is the thermolysis product of castor oil, was also employed for the oxo reaction. The linear product 11-ethoxylcarbonyl undecanal can be used for the synthesis of the musk perfumes and nylon-12. We found that the ratio of linear (n) to branched (i) aldehyde can be as high as 8, with 40% conversion to aldehydes when the ethanol volume fraction in the reaction system was 11%. The catalyst was reused in three successive runs for both reaction systems, the yields of the aldehydes and the n/i ratios remaining almost the same.

EXPERIMENTAL

Reagents

p- and *m*-Vinylbenzyl chloride and styrene (Aldrich, 99%) were passed through an inhibitor removal column before use. Ethyl 10-undecenoate (Aldrich 98%), triphenylphosphine (Aldrich, 99%), fuming sulfuric acid (Aldrich, free SO_3 content 27–33%), triethylamine (Aldrich, 99%), rhodium chloride hydrate (Johnson Matthey 99.9%), syngas (Linde, $CO/H_2 = 1$), formaldehyde (Aldrich, 37 wt% aq.), sodium hydroxide (Aldrich, 99.99%), cyclohexane (Aldrich, HPLC), and other solvents were used without further purification. Silica catalyst support (Aldrich, grade 951) and silica gel (Aldrich, TLC high-purity grade, without binder) were used as support and for the chromatographic separation, respectively.

Instruments

A 150-ml high-pressure reactor (Parr 4841) was employed for hydroformylation. Energy dispersive spectroscopy surface analysis (EDS) was performed on a PGT/IMIX field emission electron microscopy equipment. The surface functionalized silica particles were investigated with a scanning electron microscope (SEM) (Hitachi S-800) and the specific surface area was measured with a physical adsorption analyzer (Accusorb 2100E, Micromeritics). The infrared absorption spectra of the supported catalysts and of the oxo reaction products were obtained with a Mattson Alpha Centauri FT-IR instrument using a KBr cell. ^{1}H-NMR spectra of the hydroformylation products were recorded on a VXR-400 spectrometer using d-chloroform as solvent.

Preparation of the Monomer and Ligand

The *m*-, *p*-vinylbenzyl triethyl ammonium chloride (VEAC) and phosphonium chloride (VEPC) were synthesized according to reported methods (*17*). The monosulfonated triphenylphosphine (DPM) was synthesized employing the procedure of Ahrland *et al.* (*18*).

Polymerization on the Surface of Silica Particles

A powder of 2.0 g silica was introduced with magnetic stirring into an aqueous solution containing 0.6 g of VEAC, 8 mg of $K_2S_2O_8$ and 10 ml water, placed in a 50-ml beaker. Then a moderate air flow was employed to evaporate most of the water with stirring. After about 1 h of stirring, a wet yellow solid containing about 60 wt% water was obtained. The wet solid was immersed into 10 ml of decane located in a glass tube. Further, the tube was sealed with a rubber septum and Ar was bubbled through the liquid for 5 min with ultrasonic degassing. The polymerization was carried out in a water bath at 60–70°C for 12 h. The obtained quaternized silica was purified by extraction with chloroform for 20 h in a Soxhlet extractor, since both the VEAC and the unbound P(VEAC) can be washed out with $CHCl_3$. Finally, after vacuum drying, 2.6 g of surface quaternized silica were obtained {denoted as Si–P(VEAC)-(1)}. Several quat-

TABLE 1

Deposition of Poly(Quaternary Onium Chloride) on the Surface of Silica

Entry	Q^+Cl^-[a] (g, mmol)	$Q^+ Cl^-$ (mmol) / $Q^+ Cl^-$ (g) + Silica (g)[b]	Content of $Q^+ Cl^-$[c] in the quaternized silica (mmol of $Q^+ Cl^-$/g)	Percentage of $Q^+ Cl^-$ grafted to silica (%)
Si–P(VEAC)-(1)	VEAC (0.6, 2.37)	0.91	0.86	94.5
Si–P(VEAC)-(2)	VEAC (0.92, 3.64)	1.25	1.14	91.2
Si–P(VEAC)-(3)	VEAC (1.22, 4.82)	1.49	1.23	82.6
Si–P(VEPC)-(E)	VEPC (0.65, 2.41)	0.91	0.91	100
Si–P(VBPC)-(B)	VBPC (0.85, 2.40)	0.84	0.56	66.7

[a] VEAC is 3,4-vinylbenzyl triethyl ammonium chloride; VEPC is 3,4-vinylbenzyl triethyl phosphonium chloride; VBPC is 3,4-vinylbenzyl tributyl phosphonium chloride; E, ethyl; B, butyl; and Q^+ is the onium cation.
[b] Two g of silica were used in all the systems.
[c] Elemental analysis results.

ernized silica have been prepared with various amounts of the quaternary onium monomer (see Table 1).

Binding Cl(CO)Rh(DPM)$_2$ and DPM to the Quaternized Surface of Silica

The procedure is similar to that described in Ref. (*19*): a white powder of DPM (0.19 g, 0.47 mmol) was dissolved in 5 ml of an aqueous solution of formaldehyde. To this solution, 5 ml of a reddish aqueous solution of $RhCl_3$ (9.45×10^{-3} *M*) (the molar ratio of $RhCl_3$/DPM is 0.1) were added with stirring, followed by the addition of a 1 ml solution of NaOH (0.5 *M*). After 15 min, an orange-yellow solution containing the complex Cl(CO)Rh(DPM)$_2$ was obtained. Then 0.5 g of Si–P(VEAC)-(1) (containing 0.44 mmol of VEAC) were introduced into the solution with stirring. The color gradually changed from orange-yellow to yellowish. An air flow was employed to evaporate most of the water. To eliminate the unreacted formaldehyde the yellowish solid was washed twice, each time with 30 ml of ethanol–THF (v/v = 1). After filtration and vacuum drying at room temperature, 0.62 g of a yellowish powder were obtained. One gram of prepared supported catalyst contains 0.54 mmol of the DMP, 0.068 mmol of Cl(CO)Rh(DPM)$_2$, and 0.64 mmol of VEAC units.

Hydroformylation of Styrene

The supported catalyst powder (0.3 g containing 0.16 mmol of DMP, 0.021 mmol of Cl(CO)Rh(DPM)$_2$, and 0.19 mmol of VEAC units) was blended with 0.16 g of water. The wet catalyst powder, 10 ml styrene (9.1 g, 88 mmol), 40 ml cyclohexane, and 0.5 ml ethanol were added to the high-pressure reactor. The system was purged with syn-gas four times (to about 10 psi each time) with slow stirring, before reaction. Then the syn-gas was introduced until a pressure of 750 psi was achieved, which increased to 810 psi when the temperature of the reaction system became 85°C. The reactor was charged again with syn-gas as soon as the pressure fell to 650 psi. After 15 h of reaction with mechanical stirring, a colorless liquid phase was taken out from the reactor with a liquid removal tube. The yellow catalyst powder remained precipitated at the bottom of the reactor. The reaction mixture was vacuum concentrated in a rotary evaporator for 2 h at 40–50°C to remove the cyclohexane and the unreacted styrene. Finally, 8.0 g of oil-like liquid were obtained, from

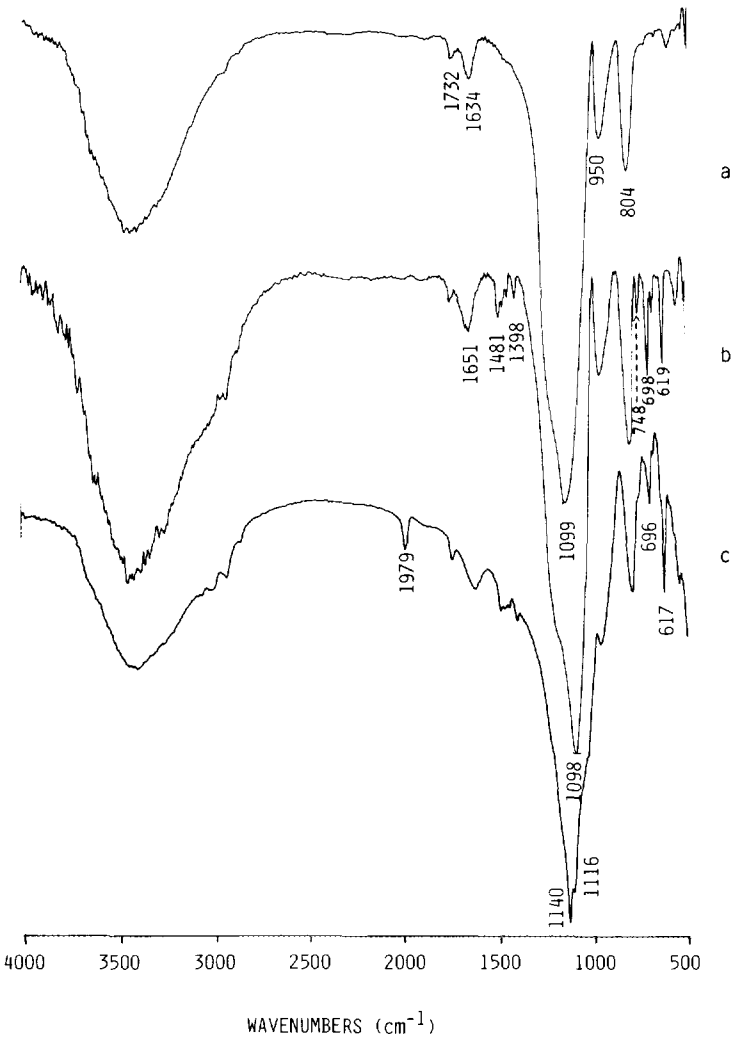

FIG. 1. (a) FT-IR spectrum of the silica substrate; (b) FT-IR spectrum of Si–P(VEAC)-(1) (the amount of deposited polymer is given in Table 1); and (c) FT-IR spectrum of the supported catalyst: Si–P(VEAC)-(1)/Cl(CO)Rh(DPM)$_2$-DPM.

which 1.4 g of polystyrene oligomers could be separated when introduced in ethanol. The ^{1}H-NMR analysis of the mixture of normal and iso phenylpropanals indicated: δ (ppm) = 2.78 (t, -C$\underline{H}_2$CHO); 3.02 (t, PhC$\underline{H}_2$-); 7.2–7.3 (m, Ph-); 9.82 (s, -C$\underline{H}$O) for normal-phenylpropanal; and δ (ppm) = 1.5 (d, -CH$_3$); 3.64 (q, -PhC$\underline{H}$<); 7.2–7.3 (m, Ph-); 9.75 (s, -C$\underline{H}$O) for iso-phenylpropanal. The ratio of normal and iso aldehydes was evaluated by the integration of the aldehyde proton signals of the n and i aldehydes.

Hydroformylation of Ethyl 10-Undecenoate

Ethyl 10-undecenoate (10.6 g, 50 mmol), 5 ml of ethanol and Si-P(VEACA)-(2) supported catalyst (0.3 g containing 0.16 mmol of DMP, 0.021 mmol of Cl(CO)Rh(DPM)$_2$, and 0.24 mmol of VEAC units) were used,

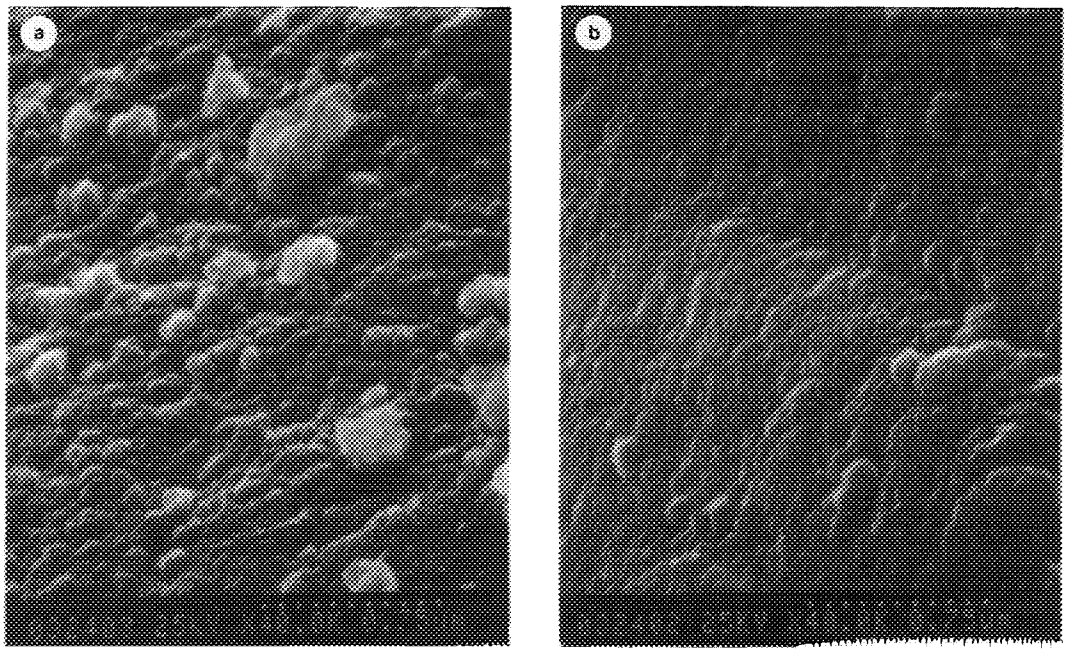

FIG. 2. Scanning electron micrographs of (a) silica and (b) quaternized silica (Si–P(VEAC)-(2) of Table 1).

the other amounts and conditions being the same as for the hydroformylation of styrene. After reaction, a colorless oil (10.7 g) was obtained. The aldehydes were separated from the unreacted olefin by vacuum liquid chromatography (*20*) using TLC silica gel as the stationary phase and mixtures of petroleum ether (30–60°C) and ethyl ether as grade eluant. 5.12 g of a mixture of aldehydes were separated, with a ratio of normal to iso products of 8, which was evaluated by both TLC and ^{1}H-NMR (comparing the integrated signals of -C<u>H</u>O). The chemical shifts are: δ (ppm) = 1.28 (m, -$(CH_2)_8$-); 1.62 (t, -$OCH_2\underline{CH_3}$); 2.26 (t, -$\underline{CH_2}CO_2Et$); 2.42 (t, -$\underline{CH_2}CHO$); 4.12 (q, -$O\underline{CH_2}CH_3$); 9.76 (s, -C<u>H</u>O) for $OHCCH_2(CH_2)_8CH_2CO_2CH_2CH_3$, and δ (ppm) = 1.08 (d, -$CH(\underline{CH_3})$CHO); 9.60 (s, -C<u>H</u>O) for the iso aldehyde. The resonance absorption of the proton -$\underline{CH}(CH_3)CHO$ is overlapped with the CH_2 absorption; the other proton resonance absorptions of $OHCCH(CH_3)(CH_2)_7CH_2CO_2CH_2CH_3$ coincide with those of the normal product.

RESULTS AND DISCUSSION

Polymerization in the Aqueous Layer Adhering to the Surface of Silica

Most of the previous investigations which used silica as substrate for immobilization of functional groups converted the surface Si–OH groups to suitable anchors through several reactions steps (*21*). In this paper, hydrophilic polymers of quaternary ammonium chloride or phosphonium chloride have been attached to the surface of silica via the polymerization of monomers in the adhering aqueous layer on silica. Silica was immersed into an aqueous solution of a quaternary onium monomer and initiator, and the suspension was concentrated by evaporating most of the water until the system remained with about 60 wt% water. This wet solid was introduced in decane, which plays the role of a heat-transfer medium and

TABLE 2

Specific Surface Area of the Silica with Surface Grafted Poly (Q^+ Cl^-)

Sample	Silica support	Si–P(VEAC)-(1)	Si–P(VEAC)-(2)	Si–P(VEPC)-(E)
Specific surface area (m^2/g)	347	215	150	250

also prevents the escape of water. Preserving a water layer on the surface of silica facilitates the polymerization process during the subsequent heating at 60–70°C for 12 h. The quaternized silica powder is finally extracted with chloroform in a Soxhlet extractor to eliminate the unreacted monomer and some of the water. A high percentage of the monomer was attached as polymer chains to the silica, as demonstrated by the elemental analysis given in Table 1. The comparison of the IR spectra (Fig. 1a) of silica and Si–P(VEAC)-(1) (Table 1) indicates that P(VEAC) is present in the porous silica (Fig. 1b). The electron micrographs (Fig. 2) allow to compare the surface morphologies of silica and quaternized silica after the deposition of P(VEAC) on its surface. One can observe that the roughness is higher on silica, which implies that the P(VEAC) chains fill the cavities of silica. This occurs because most of the water and monomer can penetrate in these cavities with the assistance of ultrasonic degassing before polymerization. The specific surface area measurements show that the inclusion of the polymer in the porous silica reduces, as expected, the specific surface area (Table 2).

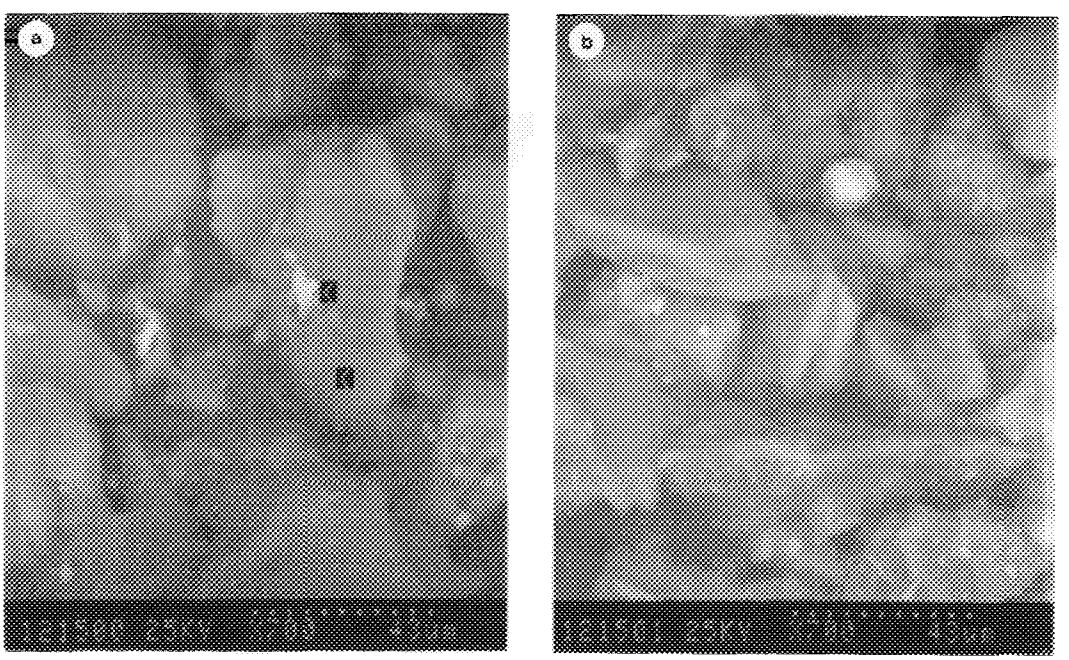

FIG. 3. (a) The backscattered electron image (BEI) of the supported catalyst: Si–P(VEAC)-(1)/Cl(CO) $Rh(DPM)_2$-DPM. (b) The BEI of the same supported catalyst after it was reused three times in the hydroformylation of styrene.

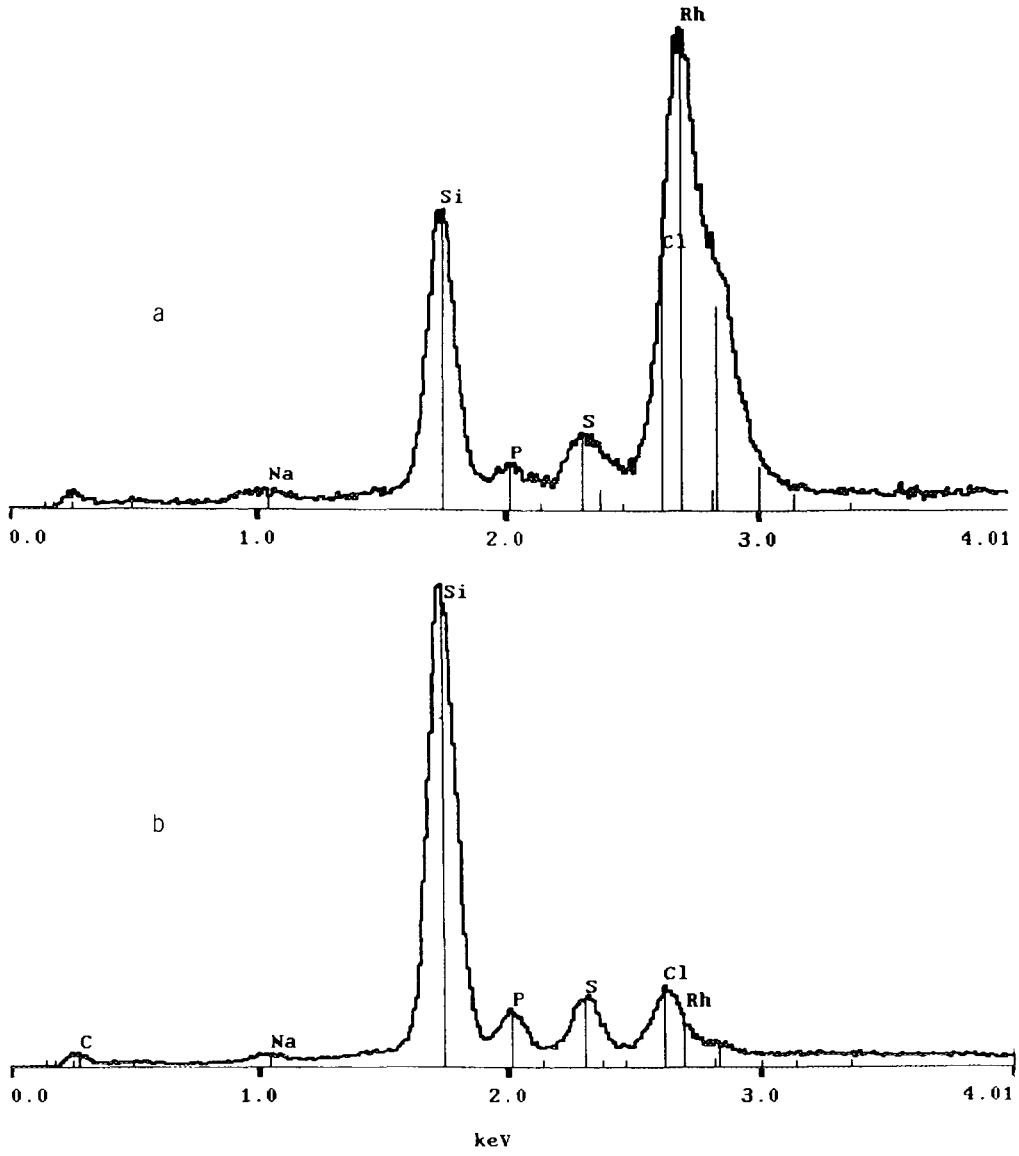

FIG. 4. (a) EDS surface elemental analysis of the white spots shown in Fig. 2a; (b) EDS surface elemental analysis of the area outside of the white spots.

Characterization of the Supported Catalyst

The synthesis of the complex H(CO) $Rh(DPM)_3$ crystals was previously (*22*) carried out by first preparing the oil-soluble complex $H(CO)Rh(PPh_3)_3$ and by treating subsequently in THF this complex with an excess amount of DPM for a few days in a refrigerator. In this paper, a single step procedure was employed to prepare the supported catalysts. The rhodium complex was synthesized in an aqueous medium, as described in the experimental section, by a procedure analogous to that used for $Cl(CO)Rh(PPh_3)_2$ (*19*). The molar ratio between DPM and $RhCl_3$ was 10. Its structure is expected to be similar to that of

TABLE 3

Hydroformylation of Styrene Catalysed Using Si–P(VEAC)-(1) Supported $Cl(CO)Rh(DPM)_2$

Reuse of the catalyst	Supported catalyst system			Styrene (mmol)	Yield of aldehyde (%)	i/n ratio
	Ligand DPM (mmol)	Complex $Cl(CO)Rh(DPM)_2$ (mmol)	Pendant Q^+Cl^- VEAC (mmol)			
1st	0.16	2.1×10^{-2}	0.19	87.7	56.5	6.2
2nd					55.2	6.6
3rd					53.8	6.3

Note. Reactions have been carried out at 85°C, 800–650 Psi, for 15 h; other conditions are listed in the Experimental section.

$Cl(CO)Rh(PPh_3)_2$. The quaternized silica powder was treated with the above aqueous solution. For Si–P(VEAC)-(1) supported $Cl(CO)Rh(DPM)_2$ and DPM, the total amount of DPM was almost equivalent to the number of pendant onium units. The DPM molecules form via their sulfonic groups ion pairs with the onium units of the polymer. Some of these ion pairs are coordinated to Rh through the bound DPM. The morphologies and compositions of the immobilized systems were investigated with SEM and EDS. The backscattered electron image (Fig. 3a) shows a number of white islands located on the silica particles. The EDS surface elemental analysis (Fig. 4) indicates that these white islands contain high concentrations of Rh complexes, while the regions outside the white spots contain much lower concentrations of such complexes. It is likely that the white islands are generated on P(VEAC) chains that are located on the cracks or larger pores of silica, since they are more easily swollen by water and thus provide a larger number of sites for ion-exchange. This leads to the formation of a large number of ion-pairs between the DPM anion and the onium cation. The FT-IR spectrum (Fig. 1c) shows a week characteristic absorption of the coordinated carbonyl group (at 1979 cm^{-1}) in the bound complex $Cl(DPM)_2RhCO$. Comparing with the corresponding IR absorption (at 1970 cm^{-1}) of the carbonyl group in the complex $Cl(PPh_3)_2RhCO$ (*19*), one can attribute this increase of the wavenumber from 1970 to 1979 cm^{-1} mainly to a weaker coordination bonding between Rh and CO in the immobilized complex than in the latter one. This is probably caused by the electron-withdrawing effect of the *meta*-substituted sulfonate group of one of the benzene rings of triphenylphosphine ligand, which reduces the σ electron donation ability of the phosphorus atom. In conclusion, there are two kinds of

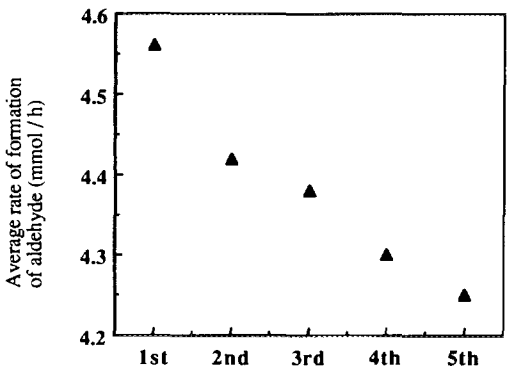

FIG. 5. Reaction conditions: (1) 0.5 g of Si–P(VEAC)-(2) as support containing 0.57 mmol of pendant VEAC units, on which 5.3×10^{-2} mmol of the rhodium complex and 0.42 mmol of DPM are immobilized. The catalytic system contains 50 wt% water; (2) 900 psi ($CO/H_2 = 1$), 85°C, 15 h for each run; (3) styrene (88 mmol) in 45 ml of cyclohexane and 0.5 ml of ethanol for each feedstock.

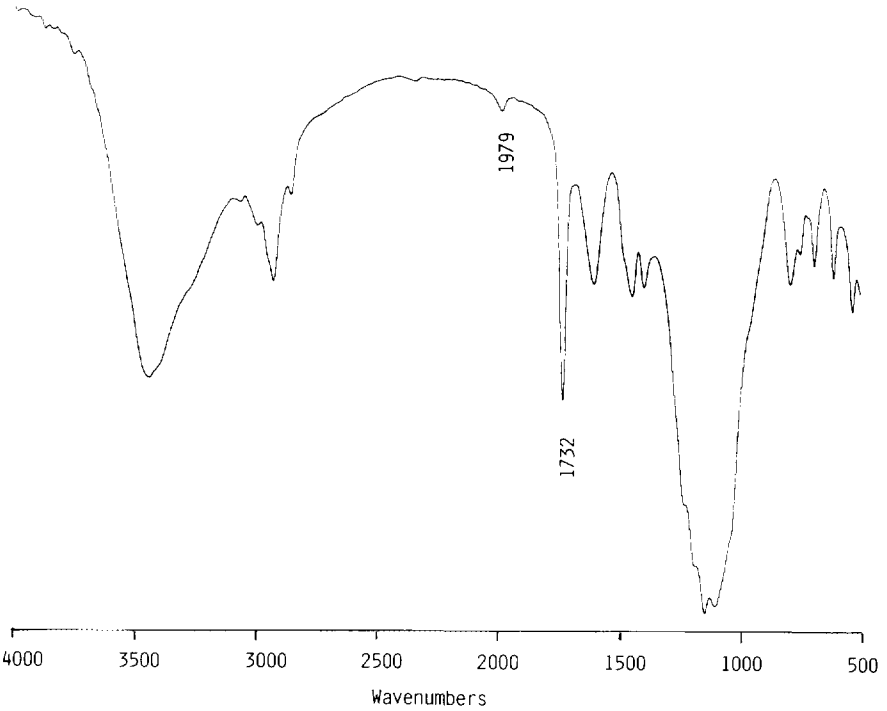

FIG. 6. FT-IR spectrum for the catalyst reused five times (the strong carbonyl absorption band at ν = 1732 cm^{-1} is due to the adsorbed aldehyde compounds).

regions on silica particles: one is covered with catalytic polymer clusters containing higher concentrations of rhodium complex, and another is covered by P(VEAC) and DPM with a much lower concentration of rhodium complex.

Hydroformylation of Functional Olefins

Styrene and ethyl 10-undecenoate are used for illustration purposes, to gain insight into the oxo reaction of aromatic and aliphatic olefins with this type of immobilized catalyst. In the hydroformylation of styrene, the ratio of the iso to normal aldehydes is greater than 6, and the turnover frequency is 156 (mol of olefin/h · mol of catalyst) (Table 3). The phosphine ligand {Ph_2 P(*m*-$C_6H_5SO_3^-$ N^+Et_3Bzl--)} being large, the complex it forms with rhodium contains only two phosphine ligands (*23*). It appears that the free volume around Rh can preferentially accommodate the secondary alkyl derivative intermediate in which the coordinated H atom attaches to the terminal carbon atom and the center Rh atom to the other carbon of the original double bond. This may be a result of the fact that the above intermediate is shorter than the primary one, but is branched.

The silica supported catalyst Si–P (VEAC)-(1) of Table 3 was hydrated before use to a 35 wt% of water-content. This water forms a thin adherent aqueous layer on the hydrophilic support. After it was reused three times, the catalyst maintained a yellow color, which indicates the presence of the complex, and the SEM micrograph (Fig. 3b) remained very similar to that before the catalyst was used (Fig. 3a). The adherent water layer allows the migration of DPM on the surface, thus providing a ligand-excess environment which prevents the decomposition of the rhodium complex. In addition, the presence of a small amount of ethanol (1.2% volume fraction of the solvent) enhances the yield of the aldehydes, which otherwise is

TABLE 4

Hydroformylation of 10-Ethyl Undecylenoate Catalysed Using Various Supported Catalysts

Entry[a]	Supported catalyst system		Olefin (mmol)	Solvent/additive[b] (ml)	Yield of aldehyde (%)	i/n[c]
	Complex $Cl(CO)Rh(DPM)_2$/DPM (mmol)	Pendant Q^+Cl^- (mmol)				
1	2.1×10^{-2}/0.16	VEAC (0.24)	50	Ch (40)/Et (0.5)	11.2	11.2
2	As above	VEPC (0.22)		Tol (40)/Et (0.5)	15	10.6
3	As above	As above		Ch (40)/Et (1.0)	32	9.2
4	As above	VEAC (0.24)		Ch (40)/Et (5.0)	42	8.0
5	Reused the above catalyst (2nd run)			As above	40	8.1
6	Reused the above catalyst (3rd run)			As above	37.5	7.9
7	2.1×10^{-2}/0.16	VEAC (0.30)		Ch (40)/Et (5.0)	19	5.8
8	As above	Unquarternized silica		As above	7.2	3.5

[a] The reaction conditions for entries 1–6 are described in the Experimental section. In entries 1 and 4–6, Si–P(VEAC)-(2) was used as substrate; in entries 2 and 3, Si–P(VEPC)-(E) was used; in entry 7, Si–P(VEAC)-(3) was used; in entry 8, silica support was used. The reaction conditions for entries 7 and 8 are 640 Psi, 6 h of reaction time; other conditions are mentioned in the experimental section.

[b] Ch = cyclohexane; Et = ethanol; Tol = toluene.

[c] The n/i ratios were evaluated from the areas of the spots of the corresponding aldehyde in TLC using a mixture of 20 ml petroleum and 5 ml ether as eluant, R_f(n) = 0.56; R_f(i) = 0.66.

only about 2%. One can speculate that the surface attached polymer coils that contain pendant catalytic ion-pairs, are swollen with ethanol molecules, thus generating sites with suitable polarity and size, able to accommodate the styrene molecules. Subsequently, the generated phenylpropanals play the role of ethanol because they can themselves swell the polymer coils. We found that less than 5% of the styrene converted to oligomer, with an IR spectrum strongly resembling that of polystyrene, terminated however with a monocarboxyl group. The absorption band of the carbonyl group is at 1726 cm^{-1}, as in an aldehyde. No hydrogenation products such as ethylbenzene were detected by GC-MS which was equipped with a fused silica PoraPLOT wide bore capillary column (0.53-mm ID, 28-m length), a 5A molecular sieve, and a high-performance capillary column (HP-1, cross-linked methyl silicone, 0.2-mm ID, 12-m length). Alcohols such as phenylpropanol were also not detected by ^{1}H-NMR. The supported Si–P(VEAC)-(2) catalyst was reused five runs in the oxo reaction of styrene, and the total yield of aldehyde divided by time is plotted in Fig. 5. The infrared spectrum of the catalyst after five runs (Fig. 6) presents an absorption band of Rh–C=O at ν = 1979 cm^{-1}. This indicates that the rhodium complexes survive after 5 reaction runs.

The hydroformylation of ethyl 10-undecenoate led to the high ratio of about 8 of normal to iso aldehydes. In contrast to the hydroformylation of styrene, in which the yield of the iso- aldehyde is higher than that of the linear one, a completely reversed regioselectivity ratio in the oxo reaction of ethyl 10-undecenoate (Table 4) occurs. The free volume around the Rh atom can in this case preferentially accommodate the primary alkyl derivative intermediate. This differs from what occurs in the case of styrene, and a possible explanation can be related to the

planarity of the benzene ring in styrene, in contrast to the flexibility of the long hydrocarbon chain in the case of ethyl 10-undecenoate. From Table 4, one can observe that with increasing ethanol content in the reaction medium the yield of the linear aldehyde decreases, but the total yield of the aldehydes increases. This probably occurs because the ethanol molecules decrease via a solvation effect the steric constraints around the coordination center, thus increasing the free volume. From entries 7 and 8 of Table 4, one can see that if the silica surface is not covered with polymer chains of quaternary onium chloride, the yield of the oxo reaction is very low. This is probably a result of the difficulty for the olefin molecules to contact the catalytic sites. The presence of the polymer increases the compatibility between catalyst and olefin.

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