Synthesis and Use as a Catalyst Support of Porous Polystyrene with Bis(phosphonic acid)-Functionalized Surfaces[1]

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The synthesis of a novel polymerizable bis(phosphonic acid) monomer, 1-(3-vinylphenyl)-propane-2,2-bis(phosphonic acid), is reported. Highly porous cross-linked polystyrenes possessing surface-supported bis(phosphonic acid) groups were obtained by copolymerization of **6b** with styrene and divinylbenzene. Two different methods were employed: first the polymerization of a bis(2-ethylhexyl) sulfosuccinate stabilized water/oil microemulsion in the presence of 6b; second the polymerization of the monomers in the presence of a pore-forming diluent. By both methods most of the functional groups were located on the pore surface. The best accessibility (75%) was obtained in the microemulsion polymerization. The porous polymer was ion-exchanged with Pd and used for the hydrogenation of 1-octene. The catalyst could be reused without regeneration and showed no sign of deactivation during 10 hydrogenation experiments.

Introduction

Porous cross-linked styrene-based polymers have gained widespread use as supports for polymer bound reagents and catalysts.[2] Today the large majority of these materials are made by chemical modification of preformed high surface area polymers. Polymerization of a functional monomer solution, the tailored monomer approach, to yield a functional porous copolymer would be a straightforward method to avoid many drawbacks associated with multistep chemical modification processes.[3] The occurrence of side reactions which incorporate impurities into the polymer is probably the most serious drawback. The main drawback of the materials functionalized ab initio by copolymerization is the fact that, depending on the relative reactivity ratios, a part of the functional groups are buried inside inaccessible cores of cross-linked nodules. The inaccessible part may become very large when formulations with enough cross-linking monomer to yield a macroporous structure is used. The location of functional species on insoluble polymer surfaces to give highly accessible regions of the cross-linked matrix is therefore of major importance in the synthesis of a porous polymer through a tailored monomer approach.

Our interest in the synthesis of polymer supports with easily accessible complexing functionalities guided us to modify some recent work concerning porous polymeric materials from microemulsions of water in styrene.[4-6] Bis(phosphonic acid) compounds have been found to form strong complexes with some metal ions.[7] In addition to use as a carrier for catalytically active transition metals, a bisphosphonate-containing polymer could also find use as metal separation media, as an extractant for removal of actinides from radioactive waste water[8] or in oral compositions.[9]

In this paper we present a synthesis of a high surface area polymer with bis(phosphonic acid) groups located on the surface. We also demonstrate that this polymer, after loading with Pd, is an active hydrogenation catalyst in the nonswollen solid state. Furthermore, we show that the polymer bound Pd complex is a stable hydrogenation catalyst that can be reused at least 10 turns without loss in activity. The resistance to leaching is also demonstrated.

Experimental Section

Materials. Styrene and divinylbenzene (Fluka) were vacuum distilled to remove the inhibitors. Vinylbenzyl chloride was obtained from Dow Chemicals and used as received. The monomer is a mixture of the meta (70%) and the para (30%) isomers. NaH was used as an 60% dispersion in oil. AIBN was recrystallized from methanol. Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT, Fluka) was used as received. Ion-exchanged water was obtained from a Millipore Milli-Q system. All solvents (Merck) were used without further purification.

Instrumentation. Size and size distribution of the microemulsion aggregates were determined with photon correlation spectroscopy using a Malvern Automeasure 4700 system. Direct-current plasma emission spectroscopy (DCP) was performed on a Spectrometrics Spectra Span III A apparatus. Energy-dispersive X-ray analysis was performed on a Princeton Gamma-Tech instrument. Diffuse reflectance Fourier transformed IR spectra (DRIFT) were recorded on a Perkin-Elmer 1710 spectrometer equipped with a Spectra Tech DRIFT unit. Mg Kα X-ray photoelectron spectra were obtained on a Perkin-Elmer XPS, PHI system, instrument. All reported binding energies are referenced to the carbon signal C_{1s} (284.5 eV). The active surface area, distribution of pore sizes and volume of pores were

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measured using a Carlo-Erba Sorptomatic 1900 apparatus. The amount of phosphorus incorporated into the polymer was calculated from the elemental analysis. ^{1}H NMR spectra were recorded on a JEOL GX-400 instrument at 400 MHz in $CDCl_3$ relative to TMS. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants are given in hertz. Mass spectra were recorded on a VG micromass 7070 E instrument working at an ionizing voltage of 70 eV.

Monomer Synthesis. *Tetraethylethenylidene bisphosphonate*: Tetraethylmethylene bisphosphonate (**1**) was prepared in 50% yield from sodium diethylphosphite and dichloromethane as previously reported.[10] From compound **1** tetraethylethenylidene bisphosphonate (**2**) was synthesized in 79% yield using the two-step procedure of Degenhardt and Burdsall.[11]

Tetraethyl ethane-1,1-bisphosphonate: Tetraethylethenylidene bisphosphonate (**2**) was hydrogenated at room temperature using 10% palladium on charcoal as the catalyst in absolute ethanol at 1 atmospheric hydrogen pressure. The hydrogen uptake ceased in 2 h. The mixture was filtrated through a silica gel, and the filtrate was concentrated in vacuum. Although the raw product was fairly pure, it was distilled at reduced pressure. From 67.5 g (0.225 mol) of compound **2** 62.2 g (92%) of compound **3** was obtained; bp 95–97 °C/0.05 mmHg; ^{1}H NMR ($CDCl_3$, 400 MHz) 4.19 (two overlapping q, 8H, OCH_2, $J_{HH} = 7.3$, $J_{HP} = 7.3$), 2.40 (tq, 1 H, CH, $J_{HH} = 7.7$, $J_{HP} = 23.2$), 1.47 (td, 3 H, CH_3CH, $J_{HH} = 7.4$, $J_{HP} = 17.1$), and 1.35 (t, 12 H, CH_2CH_3, $J_{HH} = 7.1$); MS (direct inlet), m/e_{theor} 302.1048 and m/e_{exp} 302.1062, M^+ 302.106 (15), 275 (13), 247 (8), 219 (9), 173 (42), 165 (100), 138 (25), 109 (28), 81 (18), 65 (25). FTIR (KBR) 3487, 2983, 2934, 2908, 1651, 1479, 1451, 1393, 1368, 1254, 1165, 1022, 966, 819, 737, 685, 527.

Tetraethyl 1-(vinylphenyl)propane-2,2-bisphosphonate: Tetraethyl ethane-1,1-bisphosphonate (**3**, 30.0 g, 0.099 mol) was added in portions with stirring under nitrogen to a slurry of sodium hydride (2.69 g, 0.112 mol) and dry toluene (100 mL). When the release of hydrogen ceased, the stirring was continued for an additional hour at room temperature. Then vinylbenzyl chloride (18.3 g, 0.12 mol), of which 70% was in meta and 30% para form, was added and the resulting mixture was stirred until the reaction was complete. This lasted 2 weeks at ambient temperature. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in diethyl ether, washed three times with water, dried over sodium sulphate, and concentrated again to give 33.5 g (81%) of the raw product tetraethyl 1-(vinylphenyl)-propane-2,2-bisphosphonate (**4b**), which was used without further purification in the subsequent reaction.

Tetrakis(trimethylsilyl) 1-(vinylphenyl)propane-2,2-bisphosphonate: A mixture of 33.5 g of the raw product **4b**, 150 mL of trimethylchlorosilane, 55 g (0.46 mol) of dry potassium bromide and a catalytic amount of tetrabutylammonium bromide, was refluxed vigorously with stirring under nitrogen for 2 weeks. After cooling, the solution was decanted. The solid residue was washed several times with petroleum ether (bp 40–60 °C), and the solutions were combined. The excess of trimethylchlorosilane and solvent was removed by distillation at reduced pressure and 43.3 g (91%) of raw product tetra(trimethylsilyl) 1-(vinylphenyl)-propane-2,2-bisphosphonate (**5b**) was obtained. It was used without further purification in the subsequent reaction.

1-(Vinylphenyl)propane-2,2-bis(phosphonic acid): The raw product **5b** (43.3 g) was vigorously stirred at room temperature for a few hours in 100 mL of an acetic acid–tetrahydrofuran–water (3:1:1) mixture. The solvents were evaporated in vacuum, and the solid residue was suspended in ethyl acetate. The mixture was centrifuged for 10 min at 2500–3000 rpm and decanted. The treatment was repeated several times. The solvent residues were evaporated from the solid white product and 12.0 g (54%) of pure 1-(vinylphenyl)propane-2,2-bis(phosphonic acid) (**6**) was obtained, of which about 70% was the meta-substituted compound; ^{1}H NMR (DMSO, 400 MHz) 8.6–8.1 (m, 4 H, OH), 7.38–7.16 (m, 4 H, Ar), 6.71 (dd, 1 H, $=$CH–Ar, $J_{HHcis} = 10.9$, $J_{HHtrans} = 17.6$), 5.78 (dd, 1 H, $H_{cis}C{=}C$–Ar, $J_{HHtrans} = 17.6$, $J_{HHgem} = 0.8$), 5.24 (dd, 1 H, H_{trans} $C{=}C$–Ar, $J_{HHcis} = 10.9$, $J_{HHgem} = 0.8$), 3.14 (t, 2 H, CH_2–Ar, $J_{HP} = 14.8$), 1.22 (t, 3 H, CH_3, $J_{HP} = 16.4$). The chemical shifts of para-substituted compound **6** differs from that in the following shifts; 5.79 (dd, $H_{cis}C{=}C$–Ar), 5.22 (dd, $H_{trans}C{=}C$–Ar) and 3.12 (t, CH_2–Ar). Elemental analysis: exp 42.9% C, 5.4% H, 33.5% O, 20.0% P; calc 43.1% C, 5.3% H, 31.4% O, 20.4% P.

Table I. Preparation, via the Microemulsion Polymerization Method, of Porous Cross-Linked Polystyrene Possessing Surface-Supported Bis(phosphonic acid) Groups

Nr	AOT,[a] %	water,[b] %	$P_{theoretical}$, mmol/g	$P_{analysis}$, mmol/g	access,[e] %
A1	15	5	0.58	0.48	75
A2	15	5	0.3	0.29	58
A3	15	10	0.58	0.48	62
A4	15	10	0.3	0.27	66

[a] [Bis(2-ethylhexyl) sulfosuccinate (g)]/([styrene (g)] + [DVB (g)]). [b] [H_2O (g)]/[AOT (g)] + styrene (g)] + DVB (g)]). [c] 2[1-Vinylphenylpropane-2,2-bis(phosphonic acid)(mmol)]/[monomers (g)]. [d] From elemental analysis. [e] $Cu_{complexed}/P_{analysis}$.

For the mass spectrometric analysis, the product **6b** was silylated. MS (direct inlet), m/e_{exp} 594.2002 and m/e_{theor} 594.2003 M^+ 594.200 (5), 579 (39), 369 (100), 353 (8), 237 (8), 147 (9), 77 (57).

It was not possible to determine a distinct melting point for the compounds **6**.

Polymer Synthesis. *Microemulsion polymerization*: Styrene, divinylbenzene, and **6** were copolymerized in a AOT stabilized microemulsion of water in styrene. The styrene phase had a molar ratio of divinylbenzene to styrene of 0.2/0.8. The microemulsions were prepared by slowly adding water to a styrene/DVB solution of AOT under vigorous stirring. Thus, polymer A1 (see Table I) was prepared according to the following. A microemulsion was prepared by droppvise addition of water (0.26 g) to a styrene (2.45 g, 23.52 mmol)/divinylbenzene (2.05 g, 15.71 mmol) mixture, containing 0.675 g AOT. 1-Vinylphenylpropane-2,2-bis(phosphonic acid) (0.44 g, 1.4 mmol) was added in portions to the microemulsion. The solution was thermostated to 30 °C until an optically clear microemulsion was obtained. AIBN (24 mg) was added and the test tube was sealed with a rubber stopper that was penetrated with a capillary needle. Polymerization was initiated by heating to 60 °C for 12 h. The porous polymer obtained was ground using a IKA laboratory mill fitted with a 1-mm filter and extracted overnight with methanol and toluene. After vacuum drying, the polymer was fractionated in a Vibrax VXR machine. No sulfur was detected in the polymer by energy-dispesive X-ray analysis.

Polymerization in the presence of a pore forming diluent: Short-chain alcohols, propanol, butanol, and hexanol were used as pore-forming diluents.[12] The monomer solutions were prepared by simply mixing the monomers in a test tube until the solution showed no sign of unsolubilized monomer. Thus, polymer B1 (see Table II) was synthesized according to the following. 1-Vinylphenylpropane-2,2-bis(phosphonic acid) (0.37 g, 1.19 mmol) was added to a styrene (1.97 g, 18.91 mmol)/divinylbenzene (1.65 g, 12.6 mmol) mixture, containing 2.67 g of propanol. 20 mg of AIBN was added and the test tube was sealed with a rubber stopper that was penetrated with a capillary needle. Polymerization was initiated by heating to 60 °C for 12 h. The porous polymer obtained was ground using a IKA laboratory mill fitted with a 1-mm filter and extracted with methanol and toluene. After vacuum drying, the polymer was fractioned in a Vibrax VXR machine.

Diffuse reflectance Fourier transformed IR analysis of polymers A1 and B1 showed essentially identical IR spectra with the following adsorption bands; (DRIFT, 0.06-mm fraction); 3058, 3024, 2928, 1940, 1869, 1801, 1740, 1601, 1509, 1492, 1451, 1372, 1170, 1029, 905, 832, 796, 759, 705, 547.

Determination of the Accessibility. The amount of bis(phosphonic acid) groups on the surface of the polymer was determined by the polymers ability to bind Cu^{2+} ions from a water solution. The polymer was placed in a column, treated with 1 M KOH for 3 h and was washed with water until pH 7. $CuCl_2$ solution (200 mL) containing a 10-fold excess of Cu^{2+} over

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(10) Hormi, O, E. O.; et al. *Synth. Commum.* **1990**, *20*, 1865.

(11) Degenhardt, C. R.; Burdsall, D. C. *J. Org. Chem.* **1986**, *51*, 3488.

(12) See for example ref 2a, pp 1–39.

the theoretical amount of phosphonic acid groups of the polymer was circulated through the column overnight. The polymer was washed thoroughly with water, after which Cu^{2+} was eluated from the polymer with 1 M HCl. The Cu^{2+} concentration in the acidic eluent was obtained by DCP analysis.

Loading of Palladium. The 0.125–0.5-mm fraction of the ground polymer was placed in a column, washed with 100 mL of 1 M KOH, followed by water until the effluent reached pH 7. The polymer was treated with a dilute $PdCl_2$ water solution for 3 h, and then the catalyst was washed with water and ethanol. The resulting yellow to brown polymer was suspended in ethanol, and hydrogen was passed through for 2 h. This resulted in a dark gray material.

Hydrogenation of Octene. The hydrogenations of 1-octene were carried out in a 100-mL round-bottomed flask. The vessel was immersed in a water bath thermostated to 26 °C, equipped with a magnetic stirrer, and connected to a gas burette that maintained the hydrogen pressure at constant 1 atm. The catalyst in 45 mL of methanol was placed in the reaction vessel, and the air was removed. The system was flushed several times with H_2 and leak tested at 200 mm H_2O overpressure of H_2. Then H_2 was passed through for 10 min with magnetic stirring in the presence of the catalyst to allow for hydrogen saturation. The stirrer speed was adjusted so that increasing the rate of stirring did not change the rate of the hydrogenation reaction. With the equipment used this stirrer rate was found to be 1000 rpm. The substrate, 5 mL of 0.1 M octene in methanol, was injected through a septum. The H_2 consumption was automatically recorded from the gas burette, and the conversion as a function of time was calculated. When the hydrogen consumption ceased, the catalyst was filtrated from the reaction solution, washed with methanol, and dried in vacuum. After this the catalyst was used in the next hydrogenation. An average of 1.8% of the polymer was lost in each catalytic cycle during filtration. The calculated rates are corrected to the amount of catalyst actually present in every hydrogenation.

Results and Discussion

To prepare a surface-functionalized porous polymer, where the surface functionality is a complex former, we needed to rationally design a monomer with a hydro/lipophilic balance that the monomer could be expected to be attracted to the w/o interface in a water/styrene microemulsion. The basic characteristics of such a monomer are (a) a polymerizable lipophilic group, (b) a hydrophilic group that is able to form a complex, and (c) a spacer between the two groups. As the polymerizable group we chose a styryl moiety and in order to retain a random copolymerization between styrene and the functional monomer we introduced an isolator (CH_2) between the styryl moiety and the polar electron withdrawing group. Because of its proved and sometimes unexpected characteristics as a complexing agent bis(phosphonic acid) was chosen as the polar group.

Compound (**6a**, X = H) was prepared by the procedure outlined in Scheme I. Starting from tetraethyl methylenebisphosphonate (**1**), tetraethyl 1-(vinylphenyl)ethane-2,2-bisphosphonate (**4a**, X = H) was prepared and hydrolyzed to **6a**. However, we found it impossible to obtain a non-cross-linked homopolymer from **6a** indicating that **6a** had reacted with a second molecule of vinylbenzyl chloride resulting in a bifunctional monomer, which we found difficult to avoid. To prevent the formation of a cross-linker, a methyl group was introduced in the starting material in the position to prevent the formation of the bifunctional monomer. The monomer (**6b**, X = CH_3) was prepared as outlined in Scheme I and as detailed in the experimental part. From monomer **6b**, it was possible to prepare a water soluble polymer, and this monomer was used in the subsequent polymerizations.

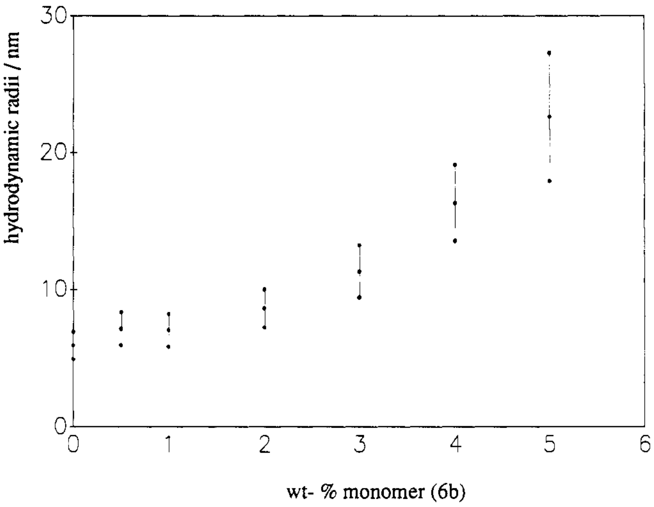
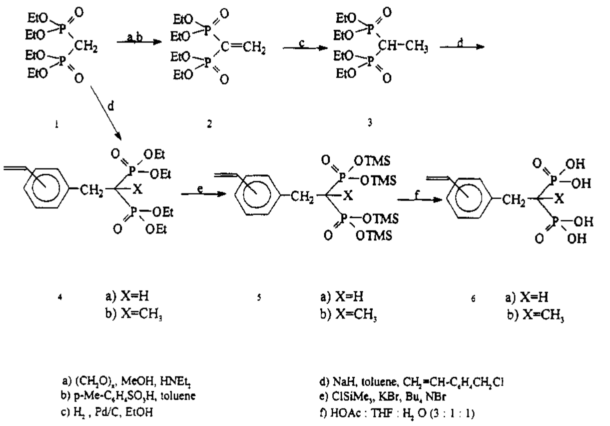


Figure 1. Hydrodynamic radii r_h and standard deviation of microemulsions formed by water and AOT in a styrene/divinylbenzene solution as a function of wt % 1-(vinylphenyl)-propane-2,2-bis(phosphonic acid) on total monomer content.

Scheme I



Two methods to prepare a surface functionalized polymer support were considered and accomplished. The major difference between the two methods is the behavior by which the polar groups enter the surface of the polymer (see Figures 2 and 3).

Terpolymerization of 1-vinylphenylpropane-2,2-bis(phosphonic acid), styrene, and divinylbenzene was complicated by the fact that the bis(phosphonic acid) monomer was completely insoluble in the styrene monomers. However, the monomer was quite soluble in a water/AOT/styrene–DVB microemulsion. For example it is possible to solubilize up to 15 wt % 1-vinylphenylpropane-2,2-bis(phosphonic acid) on total monomer content in a 5 wt % water, 15 wt % AOT microemulsion. These values are remarkably high compared to the fact that pure water can solubilize only up to 10 wt % 1-vinylphenylpropane-2,2-bis(phosphonic acid) and a solution of 15 wt % AOT in styrene not at all. We reasoned that this behavior might be due to the ability of the bis(phosphonic acid) monomer to act as a cosurfactant in the microemulsion system. Light-scattering experiments on the w/o microemulsion (Figure 1) supported our assumptions. On increasing the content of 1-(vinylphenyl)propane-2,2-bis(phosphonic acid) the reverse micelles in the system transform into somewhat larger but still narrow-sized aggregates of a Gaussian size distribution.

After polymerization, porous solids with bisphosphonic acid as surface groups are obtained. The reacting microemulsions became progressively more opaque with no apparent phase separation. The reverse micelles in the

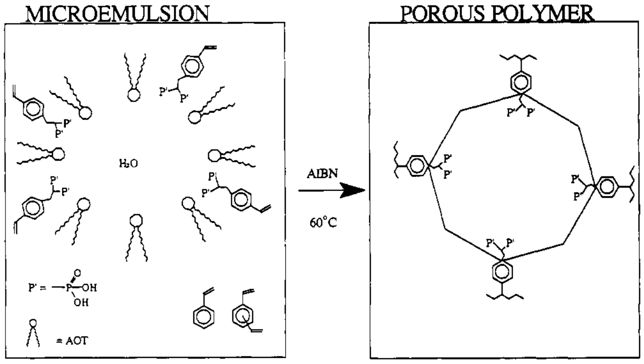


Figure 2. Polymerization of a water/AOT/(styrene–DVB) microemulsion in the presence of a functional cosurfactant.

system assemble to some degree during polymerization to form a structure of interconnected pores to which the functional cosurfactant will be anchored (Figure 2). The $-SO_3^-$ groups of the surfactant AOT may affect the metal binding properties of the polymer if the surfactant is not properly washed out or if the surfactant attach to the matrix by a chain-transfer reaction. The absence of sulphur (as obtained by energy-dispersive X-ray analysis) was taken as a proof that the surfactant was successfully removed from the polymer. The amount of bis(phosphonic acid) groups on the surface of the polymer was determined by the polymers ability to bind Cu^{2+} ions from a water solution. DCP analysis of Cu^{2+} in the acidic eluents, together with elemental analysis of phosphorus confirmed that a very high degree of the acid groups are present on surfaces available to the aqueous Cu^{2+} solution. XPS studies on the resins after NaOH treatment as well as after ion exchange with Cu^{2+} gave a Na/P and Cu/P ratio of 1, respectively. The composition of the microemulsions employed and the degree of accessible bisphosphonic acid groups in the polymers are presented in Table I.

1-(Vinylphenyl)propane-2,2-bis(phosphonic acid) is soluble in most short-chain alcohols. Many such alcohols may be used as pore-forming diluents in the synthesis of porous polystyrene materials used for example as separation media. A suitable diluent should be a solvent for all the monomers but a nonsolvent for the formed polymer. The polymerization of styrene and cross-linker in the presence of a pore-forming diluent proceeds through a rapid phase separation at the point where the diluent no longer can solubilize the formed polymer. If the bis(phosphonic acid) monomer is added to this diluent, we would expect to see a concentration of bisphosphonic acid groups to the alcohol rich pores formed during the phase separation (Figure 3). That this actually happens is shown by quantitative assessment of the metal complexation (by elemental analysis of the polymer and DCP analysis of the Cu^{2+} solutions) presented in Table II.

Table II. Preparation, via Polymerization in the Presence of a Diluent, of a Porous Cross-Linked Polystyrene Possessing Surface-Supported Bis(phosphonic acid) Groups

Nr	diluent, wt %	P_{theor},[a] mmol/g	$P_{analysis}$,[b] mmol/g	access,[c] %
B1	propanol 40%	0.6	0.59	43
B2	butanol 40%	0.6	0.55	40
B3	hexanol 40%	0.6	0.51	34
B4	butanol 50%	0.8	0.33	65

[a] 2[1-Vinylphenylpropane-2,2-bis(phosphonic acid) (mmol)]/[monomers (g)]. [b] Amount of phosphorus from elemental analysis. [c] $Cu_{complexed}/P_{analysis}$.

Although the second method gave lower accessibilities than the microemulsion polymerization, it is obvious that the bis(phosphonic acid) groups indeed are attracted toward the polymer alcohol interface formed during polymerization. Thus, this orientation seems to be more pronounced with short-chain alcohols. The degree of functionalization is restricted by the solubility of the comonomer, 1-(vinylphenyl)propane-2,2-bis(phosphonic acid), in the alcohol phase. Higher amounts of diluent makes it possible to solubilize more bis(phosphonic acid) monomer in the system, but unfortunately this also lowers the copolymer yield considerably. This is probably due to the formation of soluble 1-(vinylphenyl)propane-2,2-bis(phosphonic acid) homopolymer or oligomer in the alcohol filled pores formed after phase separation.

Polymer A1 (Table I) was loaded with palladium as described in the Experimental Section earlier and used for the hydrogenation of 1-octene. To be sure that palladium binds to the bis(phosphonic) acid groups and that attachment to the polymer matrix does not take place, we have tested the reaction of palladium with a polymer identical with A1 but without monomer **6** under the same

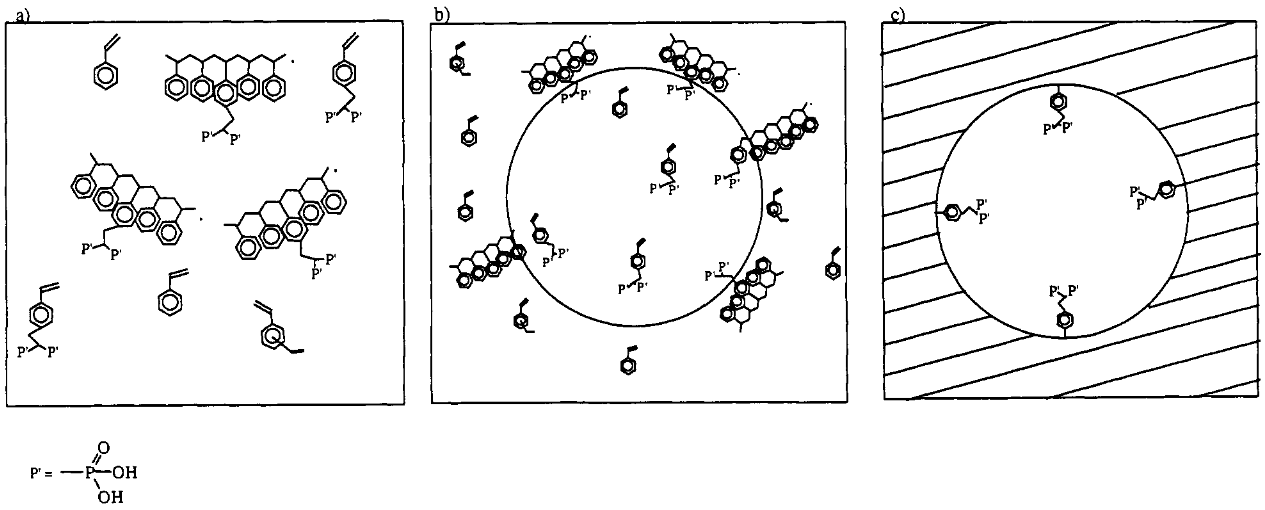


Figure 3. Schematic illustration of the polymerization of styrene, divinylbenzene and 1-(vinylphenyl)propane-2,2-bis(phosphonic acid) in the presence of a pore forming diluent. (a) An early stage of the polymerization process. (b) The functional monomer and bis(phosphonic acid)-rich segments will be concentrated in the alcohol-filled pores after phase separation have occurred. (c) A porous structure with the acidic groups anchored to the surface have been formed.

Table III. Half-Lives and Rates for 10 Hydrogenations of Octene with the Same Polymer-Supported Pd Catalyst

	no.[a]								
	1	2	3	4	5	6	7	8	9
m_{kat}/mg	131	130	126	126	115	110	109	108	107
$t_{1/2}{}^{c}$/min	12	10.5	12	13.5	13.5	14	16.5	14	15
r^{d}/mL (min g)	0.7	0.83	0.65	0.65	0.71	0.69	0.7	0.7	0.71

[a] Number of hydrogenation experiment using the palladium loaded polymer A1. [b] Mass of catalyst present in the hydrogenation reaction. [c] The time until 50% of the theocratical hydrogen consumption is reached. [d] Hydrogen consumption in mL/min per gram catalyst.

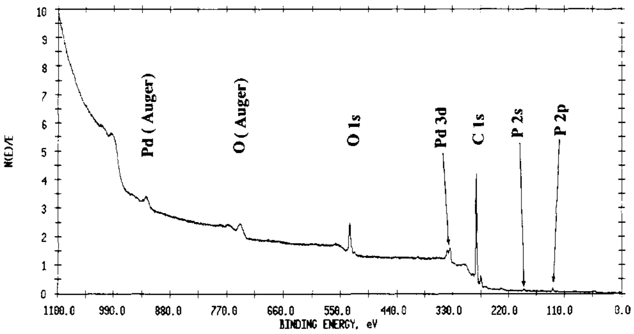


Figure 4. XPS survey spectrum of the Pd-loaded polymer.

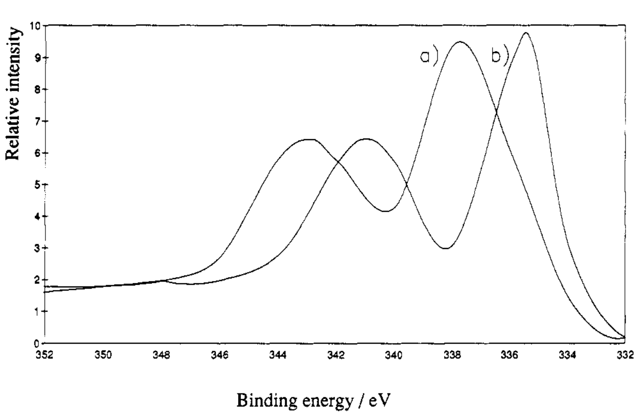


Figure 5. Pd 3 d XPS spectra of (a) fresh catalyst and (b) activated or recovered catalyst.

reaction conditions. The sample was washed with water, and a white polymer and a dark solution were obtained. No palladium was detected in the polymer (by energy-dispersive X-ray analysis). Neither did this polymer show any catalytic activity for the hydrogenation of octene.

According to BET adsorption analysis, the porous polymer-supported catalyst had a surface area of 16.7 m^2/g. The pore volume distribution calculated from the adsorption/desorption isotherm shows a quite narrow distribution of approximately 250-Å pores. The XPS spectrum of the catalyst (Figure 4) before activation showed well-resolved spin doublets with Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies at 338.1 and 343.5. The measured binding energies correspond to what is normally found for polymer bound Pd(II) complexes.[13,14] The color of the polymer-bound catalyst changes during activation from brown to dark gray. In the XPS spectrum of the activated catalyst, the Pd 3d bands are more narrow and shifted 2.3 eV toward lower binding energy (Figure 5).

These values are in good agreement with a quantitative reduction of Pd(II) to palladium metal. Atomic concentrations of phosphorus and palladium on the surface of the fresh catalyst was calculated, using the instruments software routines, from the Pd 3d (338.1, 343.5 eV) and P 3p (135 eV) peeks. The atomic concentration of phosphorous was found to be 2.2%. The palladium concentration was 2.0%. A palladium to phosphorous ratio of one was found if polymer A2 with less bis(phosphonic acid) was used. The atomic concentration of both palladium and phosphorous on the surface of this polymer was 1.5%.

The hydrogenation of 1-octene was carried out in the presence of the polymer-surface supported Pd catalyst under an atmospheric pressure of hydrogen. A total conversion of octene to octane was checked with GC analysis. Half lives and rates, calculated from the hydrogen consumption curves, are presented in Table III. The calculated rates are corrected to the amount of catalyst actually present in every hydrogenation.

No significant loss of activity could be detected during 10 hydrogenation cycles. No palladium could be detected with DCP analysis of the reaction solutions after the supported catalyst was removed by filtration ($c_{Pd} < 0.05$ ppm). Neither could any change in the Pd/P ratio be detected with energy-dispersive X-ray analysis when the catalyst was analyzed after 1.5, and 10 hydrogenations (Pd/P = 0.65).

No attempts to optimize the performance of the reusable, nonpyrophoric and nonleaking hydrogenation catalyst was made in this work.

Conclusions

Porous poly[styrene–DVB–1-(vinylphenyl)propane-2,2-bis(phosphonic acid)] have been prepared by employing two different methods. Polymerization of a bis(2-ethylhexyl) sulfosuccinate stabilized w/o microemulsion in the presence of **6b** and polymerization of the monomers in the presence of a pore forming diluent. With these methods it is possible to combine high accessibility of the functional group with the many advantages of a "tailored monomer" approach to a polymer supported catalyst. Many useful properties are obtained. (1) Most of the bisphosphonic acid groups will reside on the polymer surface where they can perform in the nonswollen solid state. (2) A minimum of polymer-bound impurities, normal methods of analysis can be used to ensure the purity of the functional monomer. (3) A rigid macroporous structure suitable for continuous-flow processes.

1-(Vinylphenyl)propane-2,2-bis(phosphonic acid)seems to be a monomer very well suited for the preparation of a support for a transition metal. The polymers reported herein could also find use in metal ion separations, in hydrometallurguical applications, in removal of heavy metals or in separation of actinides from radioactive waste.

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