Catalytic Oxidation of Organic Substrates Using a Reusable Polystyrene-Anchored Orthometallated Palladium(II) Complex

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ABSTRACT: A new heterogeneous secondary amine Pd(II) complex anchored to macroporous polystyrene beads, P-[Pd$_2$(seam)$_2$(OAc)$_2$] (seam = secondary amine), was synthesized by reacting polymer-anchored secondary amine with palladium acetate in acetic acid medium. The structure of this immobilized complex has been established on the basis of scanning electron microscope, thermogravimetric analysis, elemental analysis, atomic absorption spectroscopy, and spectrometric methods like diffuse reflectance spectra of solid and Fourier transform infrared spectroscopy. The catalytic activity of the Pd-complex was investigated toward the oxidation of various olefins and alcohols in presence of *tert*-butylhydroperoxide as an oxidant. The effects of various parameters such as solvent, oxidant, reaction time, reaction temperature, amount of catalyst, and substrates-to-oxidant ratio have been studied. The catalytic results reveal that the present polymer-anchored Pd(II) complex can be recycled more than seven times without much loss in the catalytic activity. Comparative studies have been done with the corresponding unsupported metal complex. The polymer-anchored catalyst was found to be superior to its homogeneous counterpart in activity, product selectivity, stability, and reusability © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 52–62, 2010

Key words: catalysis; polystyrene; oxidation; recycling; orthometallated Pd(II) complex

INTRODUCTION

Catalytic oxidation is a key technology for converting petroleum-based feed stokes to useful chemicals of a high oxidation states such as alcohols, carbonyl compounds, and epoxides.[1–5] Nowadays, governmental projects and new legislations demand large investment in green chemistry procedures and environmental friendly technologies. One of the most interesting areas in catalysis is the development of inorganic–organic hybrid materials for catalytic oxidation reactions.[6,7] Transition metal complex-catalyzed oxidation of organic substrate is gained importance as a viable alternative to the environmentally hazardous metal oxide-based reagent.[8–12]

Homogeneous catalyst has gained enormous relevance in various organic reactions. This type of catalyst provides high reaction rates and high turnover no. (TON) and often affords high selectivity and yields. However, homogeneous catalyst has a number of drawbacks, in particular, the problem of recycling of the catalyst. This leads to the loss of metal and ligands and incorporates impurities in the products.[13,14] To address these problems, heterogenization of homogeneous catalyst is a promising option. Various strategies such as encapsulation in zeolites,[15,16] immobilization in porous alumina,[17] immobilization in mesoporous silica,[18–20] hydrotalcite,[21] and grafting on polymers[22] have been developed in terms of heterogenization of homogeneous catalysts. Immobilization of the homogeneous catalysts through covalent bonding with polymer support is one of the most specialized methods amongst the reported heterogenization of homogeneous catalysts because polymer support enhances the thermal stability, selectivity, recyclability, and easy separation of the catalyst from reaction products leading to the operational flexibility.[23,24]

Interest in the preparation of active transition metal complexes immobilized on polymer matrix originated with efforts to develop industrially competitive homogeneous catalysts. Among them, palladium complexes are remarkably versatile reagents for the selective oxidation of organic compounds.[25–30] Selective catalytic oxidation is an important industrial

reaction because of their use in the synthesis of a wide variety of fine chemicals[31] and as flexible intermediates and precursors to many useful chemical products[32] as well. Among the catalytic oxidation product of styrene, benzaldehyde is an important organic intermediate in the industry of perfumery, pharmaceutical, dyestuff, and agrochemicals.[33] Acetophenone is used as a component of perfumes and as an intermediate in pharmaceuticals, resins, alcohols, esters, aldehydes, and tear gas. The oxidation of cyclohexene is the key reaction in the synthesis of adipic acid, which is an essential precursor in the production of nylon 6 and nylon 66.[34]

In this work, we reported the synthesis and characterization of orthometallated secondary amine Pd(II) complex anchored to macroporous polystyrene beads and tested its catalytic activity in the oxidation of several olefins and alcohols using TBHP as the oxidant. Comparative studies have been done with the corresponding unsupported metal complex to investigate the effect of anchoring of the metal complex on polymer supports toward its catalytic activities. The experimental results reveal that the anchoring of metal on solid support not only exhibits improved catalyst activity, stability, and selectivity of the product but also enables easy recovery and reuse of the catalyst.

EXPERIMENTAL

Materials and instrumentations

Analytical grade reagents and freshly distilled solvents were used throughout the investigation. The chemical analysis was done by the usual procedure.[35] Macroporous polystyrene beads, crosslinked with 2% divinylbenzene (mean pore size 46 Å, particle size 200–400 mesh sphere, surface area 1100 m²/gm) were supplied by Aldrich Chemical Company, U.S.A. Palladium(II) acetate (Pd(OAc)₂), was purchased from Arora Matthey. Alkenes, aromatic compounds, and solvents were obtained from Merck or SRL. All solvent and chemicals were analytical grade, commercially available, and used as such without further purification.

A Perkin-Elmer 2400C elemental analyzer was used to collect microanalytical data (C, H and N). BET surface areas of the samples were obtained from nitrogen adsorption/desorption isotherms by using a Beckman Coulter SA3100 surface area analyzer at 77 K. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The FTIR spectra of the samples were recorded from 400–4000 cm⁻¹ on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e.

Diffuse reflectance UV–Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Palladium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

Oxidation procedure

Liquid phase oxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and placed in an oil bath under vigorous stirring. Acetonitrile, methanol, ethyl acetate, and dichloromethane were used as solvents. The oxidant was added immediately before the start of the reactions. Substrates (5 mmol) were taken in 10 mL solvents for different sets of reactions together with 40 mg catalyst, to which 10 mmol of oxidant was added. When the reaction was carried out under O₂ atmosphere, oxygen was purged into the flask continuously. The temperature of the reacting solution was maintained constant by immersing the flask in a constant temperature oil bath and stirring the solution vigorously with the help of a magnetic stirrer. Aliquots of the reaction mixture were withdrawn at various time intervals, and the products were analyzed by using Varian 3400 gas chromatograph (GC) equipped with a 30m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified and estimated by using an Agilent GC-MS (QP-5050 model).

Preparation of catalyst

The outline for the preparation of polystyrene-anchored orthometallated Pd(II) complex, P-[Pd₂(seam)₂(OAc)₂] (P = polystyrene backbone and seam = secondary amine) is shown in Scheme 1.

Preparation of p-nitro polystyrene (2)

The suspension of macroporous polystyrene beads (5.0 g) in a mixture of acetic anhydride (20 mL), nitric acid (∼70%, 2 mL), and glacial acetic acid (4 mL) was constantly stirred for 30 min at 5°C and for 5 h at 50°C.[36] The corresponding p-nitro polystyrene was washed successively with acetic acid, water, and methanol and finally dried under vacuum.

Preparation of p-amino-polystyrene (4)

A mixture of acetic acid (20 mL), stannous chloride (5 g), concentrated hydrochloric acid (6 mL), and the suspension of p-nitropolystyrene (5.0 g) was stirred for 72 h at room temperature to reduce the nitro compound to the corresponding amine hydrochloride (3).[36] The residue was washed several times with
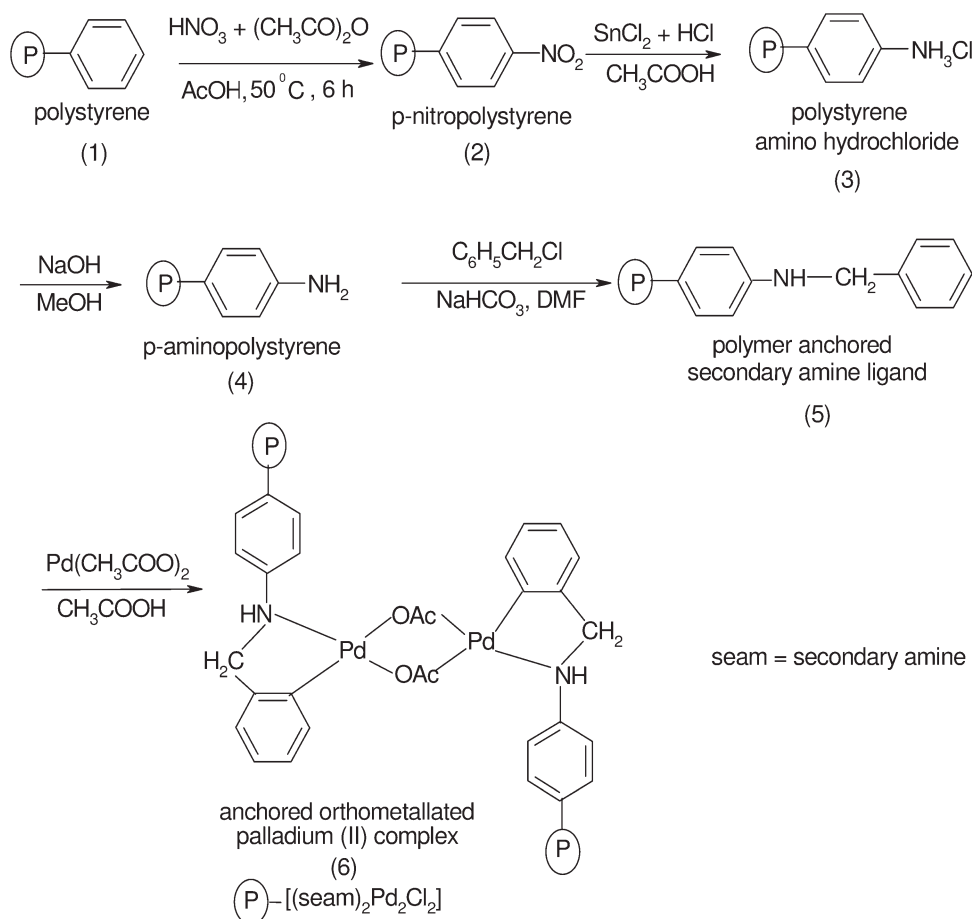
Scheme 1 Synthesis of polymer-anchored Pd(II) secondary amine complex.

hydrochloric acid (12M) and glacial acetic acid (1 : 4) mixture and then with methanol. The product on repeated treatment with dilute alcoholic NaOH (5%) produced the corresponding free amine. This was washed with alcohol and dried under vacuum.

Preparation of polymer-anchored secondary amine ligand, P-(seam) (5)

The suspension of polymer-anchored amine (5 g) in dry DMF solution (20 mL) and pure sodium hydrogen carbonate (1.75 g) was placed in a round bottom flask (100 mL). Freshly distilled benzyl chloride (1.9 mL) was added drop-wise (about 1 h) into the reaction mixture kept at 90–95°C under a vigorous stirring condition.[37] The reaction mixture was refluxed for 24 h until the polymer suspension turned into light yellow in color. The resulting polymers were washed successfully with DMF, alcoholic KOH (1M), THF, methanol and finally dried in room temperature under vacuum.

Preparation of P-[Pd$_2$(seam)$_2$ (OAc)$_2$] (6)

The yellow suspension of secondary amine (1.0 g) was taken in glacial acetic acid solution in round

bottom flask. In the reaction mixture, Pd(II) acetate (0.75 g) was added under constant stirring. Then, the reaction mixture was refluxed for 24 h until the suspension slowly changed to brown. The complex thus formed was filtered and washed thoroughly with glacial acetic acid, dry ethanol and dried in room temperature under vacuum.

Characterization of the complex

The functionalized polymer-anchored Pd(II) complex is insoluble in all common solvents. Therefore, their structural investigations were limited to the physico-chemical properties, chemical analysis, SEM, TGA–DTA, IR, and UV spectral data. Elemental analyses of the ligand and metal complex support the formulation of the complex as proposed (Table I). Metal content of the catalyst determined by atomic absorption spectroscopy (AAS) suggests 6.42 wt % Pd in the immobilized metal complex.

Scanning electron micrographs (SEM) for polystyrene, aminopolystyrene, polystyrene-anchored secondary amine ligand and metal complex were recorded to understand the morphological changes occurring at various stages and the images are

TABLE I
Analytical and Infrared Spectral Data of the Functionalized Polymers and Pd(II) Complex

Compound	Color	Cl %	C %	H %	N	Pd	C—H	δNH$_2$	ν NH$_3$Cl	ν NO$_2$ (cm^{-1})	Orthometallation	νCOO	νC—N
P	Colorless		92.50	7.60	–		3085,2810 1500,1460						
P-NO$_2$	Light yellow		74.10	5.69	6.01		3085,2810 1500,1460			1520(w) 1350(w)			
P-NH$_3$Cl	Yellow	13.25	72.01	6.72	5.81		3085,2810 1500,1460		2550	1520(w) 1350(w)			
P-NH$_2$	Pale yellow		84.12	7.34	6.72		3085,2810 1500,1460	1626(sh)		1520(w) 1350(w)			
P-[NHCH$_2$ C$_6$H$_5$]	Yellowish brown		86.14	7.18	5.26		3085,2810 1500,1460			1520(w) 1340(w)			1268
P-[(NHCH$_2$ C$_6$H$_4$) Pd(OAc)]$_2$	Deep brown		72.26	6.03	4.45	6.42	3090,2810 1500,1462			1525(w) 1340(w)	720	1580 1425	1268

presented in Figure 1. Scanning was done at 10 μm range across the length of the polymer beads. Smooth surface of the polymer beads is roughened on functionalization with amine and benzylchloride. A clear change in morphology of the secondary amine ligand after introduction of metal was observed by SEM image and suggesting the loading of palladium metal on the surface of the polymer. After metal loading, spherical shapes of the particle is quite visible throughout the specimen. Energy dispersive X-ray analysis (EDX) was carried out taking single beads of pure polystyrene, polymer-anchored ligand, and polymer-anchored metal complex. The EDX data also support that the attachment of palladium metal on the surface of the polymer matrix in the metal complex. The EDX profiles of representative samples are presented in Figure 2.
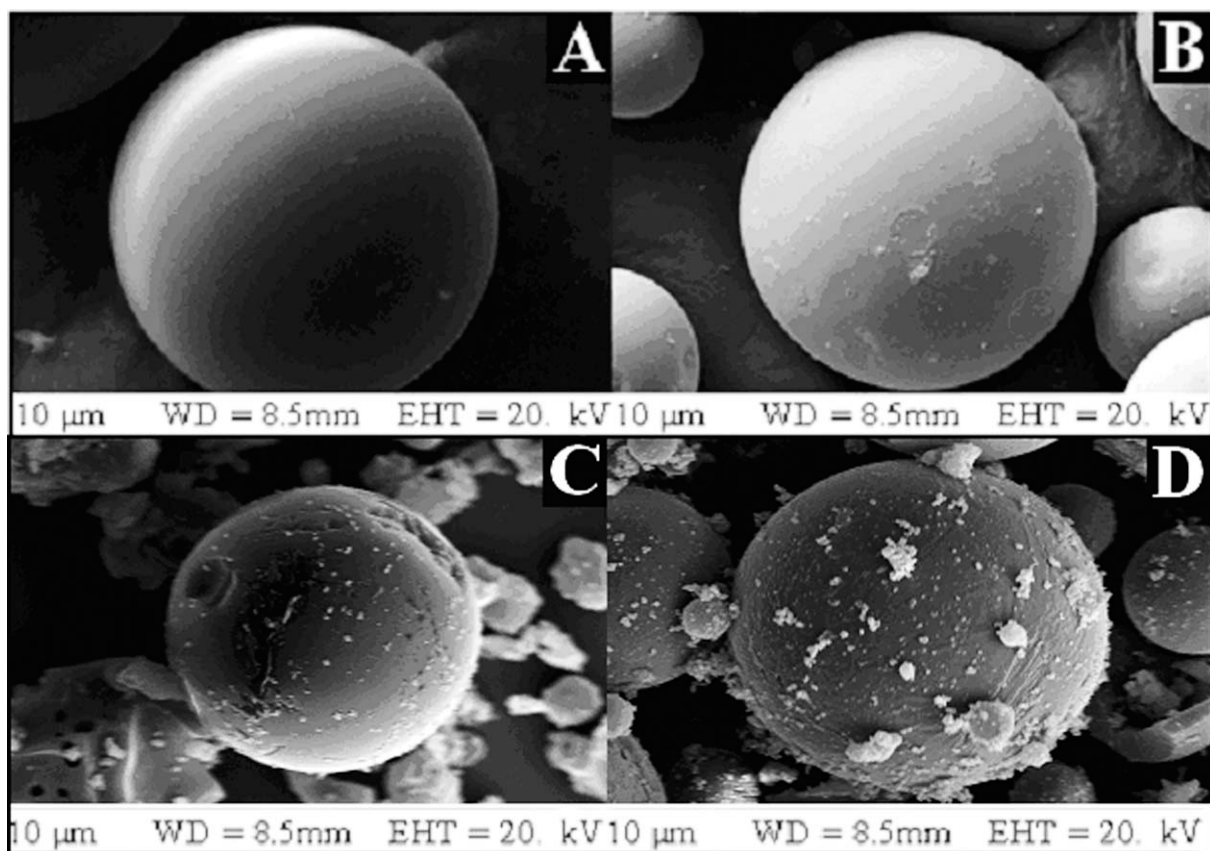

Figure 1 FESEM images of polystyrene (A), amino polystyrene (B), polymer-anchored secondary amine ligand (C), and polymer-anchored Pd(II) secondary amine complex (D), respectively.
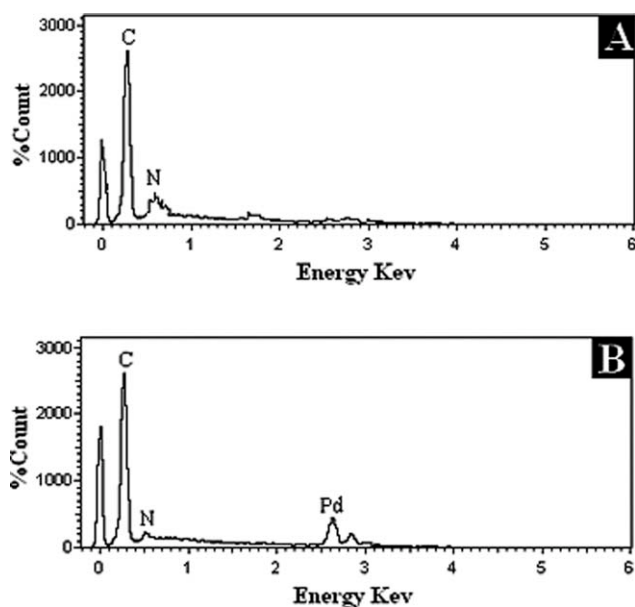
Figure 2 EDX spectra of polymer-anchored secondary amine ligand (A) and polymer-anchored Pd(II) secondary amine complex (B), respectively.

The nitrogen sorption experiments showed that the polystyrene 2% crosslink with divinyl benzene has the BET surface area (A_{sBET}) of 1.9 m^2 $g^{-1}$and the primary pore volume (V_p) of 0.009 cm^3 g^{-1}. The average pore diameter is calculated to be 7.8 nm for polystyrene. The N_2 adsorption isotherm, as well as pore size distribution of the Pd(II)-polystyrene complex, was considerably different from that of polystyrene. Pd(II)-polystyrene complex displays a considerably higher BET surface area in comparison to the polystyrene which might be due to functionalization of the polymer with bulky ligand.[38,39] The BET surface area of polymer-anchored Pd(II) complex was 3.890 m^2 g^{-1}, while the pore volume (V_p) was 0.008 cm^3 g^{-1} and pore diameter 5.5 nm.

The IR spectra of macroporous polystyrene beads exhibit peaks in the region 3100–2800 cm^{-1} (ν C—H), 1500 cm^{-1} and 1460 cm^{-1} (skeletal vibrations), 760 cm^{-1} and 680 cm^{-1} (C—H bending) (Table I). The chemical analysis of P-NO_2 suggests 56% nitration of the polystyrene ring, which is supported by the appearance of two new medium intensity peaks at 1520 cm^{-1} and 1350 cm^{-1} (ν NO_2). Another peak at 835 cm^{-1} suggests para-nitration.[36] The reduction of P-NO_2 to the corresponding P-NH_3Cl was done by the ($SnCl_2$ + HCl) procedure.[36] An estimation of chloride and nitrogen in P-NH_3Cl suggest ~90% reduction of P-NO_2 which is also supported by the reduced intensity of ν NO_2 peaks and the appearance of a new peak at 2550 cm^{-1} due to NH_3Cl.[36] After amination, two broad peaks at around 3360 and 3228 cm^{-1} and a sharp peak at 1626 cm^{-1} which are typical of the N—H stretching (ν NH_2) and bend-

ing modes (δ NH_2) in primary amines, appeared. The formation of secondary amine ligand in the next step has been confirmed by the appearance of a new characteristic peak at ~1268 cm^{-1} (ν C—N) in (5). This indicates the reaction of the NH_2 group with benzyl chloride to produce the corresponding secondary amine ligand. The polystyrene-anchored secondary amine complex of Pd(II) (6) exhibits strong IR peak at 3280 cm^{-1} (ν N—H), a medium intensity peak at 1268 cm^{-1} (ν C—N), two peaks at 1580 cm^{-1} and 1425 cm^{-1} (ν COO bridged), 450 cm^{-1} (ν Pd-N), and a relatively weak peak at 720 cm^{-1} (orthometallation).[40]

The electronic spectrum of the polymer-anchored Pd (II) complex has been recorded in diffuse reflectance spectrum mode as $BaSO_4$ disc due to their solubility limitations in common organic solvents (Fig. 3). Generally, the electronic spectrum of such low-spin Pd(II) complex may exhibit three spin-allowed d-d transitions from lower lying d orbital to higher empty d_x^2-$_y^2$ orbital, which may be designated as $^1A_{1g}\rightarrow^1A_{2g}$, $^1A_{1g}\rightarrow^1B_{1g}$ and $^1A_{1g}\rightarrow^1E_g$ transitions.[41] The present Pd(II) catalyst shows a broad spectrum with few shoulders at a region of 210–420 nm. The absorption maxima around 280 nm may be attributed to $\pi\rightarrow\pi^*$ transition. The bands around 420 nm and 350 nm may be assigned as $^1A_{1g}\rightarrow^1A_{2g}$ and $^1A_{1g}\rightarrow^1B_{1g}$ transitions, respectively.[42,43]

TGA–DTA curves of polymer-anchored Schiff base ligand and supported catalyst are shown in Figure 4. TGA was carried out in an air atmosphere with a heating rate of 10°C min^{-1} over a temperature range of 30–600°C. TGA demonstrates that polymer-anchored palladium complex degrades at considerably high temperature like the precursor polymer-anchored secondary amine ligand. DTA study reveals that all the decomposition stages are exothermic in
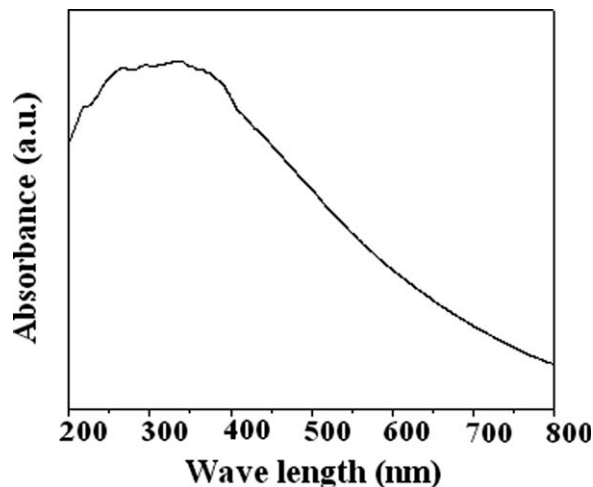

Figure 3 DRS–UV–visible absorption spectra of polymer-anchored Pd(II) secondary amine complex.
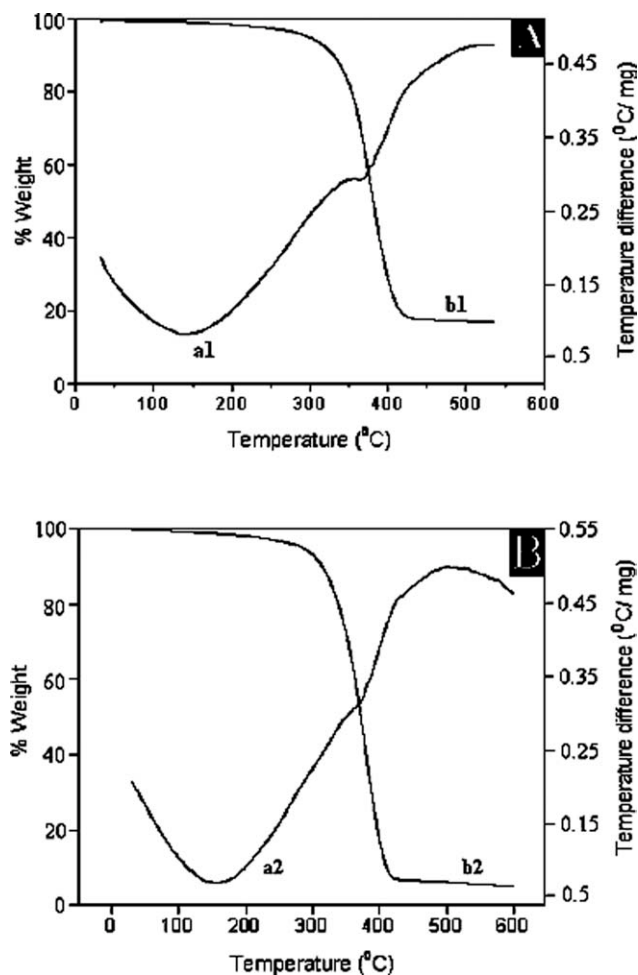
Figure 4 Differential thermal analysis (a1 and a2) and thermogravimetric weight loss (b1 and b2) plots for polymer-anchored secondary amine ligand and polymer-anchored Pd(II) secondary amine complex catalyst, respectively.

nature. The polymer-anchored palladium complex is stable upto 300°C and above which it decomposes.

Based on the above results of elemental analysis, IR, electronic spectra, and thermal analysis, the structure of the anchored orthometallated Pd(II) complex is suggested and given in Scheme 1.

RESULTS AND DISCUSSION

The catalyst P-[Pd$_2$(seam)$_2$(OAc)$_2$] was found to be highly efficient for the catalytic oxidation of olefins and alcohols. In search of suitable reaction conditions to achieve the maximum oxidation products, initial catalytic test was carried out for the oxidation of styrene and cyclohexene with polymer-anchored Pd(II) catalyst (scheme 2). Various parameters such as solvent, oxidant, reaction time, reaction temperature, amount of catalyst, and substrates-to-oxidant ratio were varied to optimize the reaction condition to get maximum oxidation products.
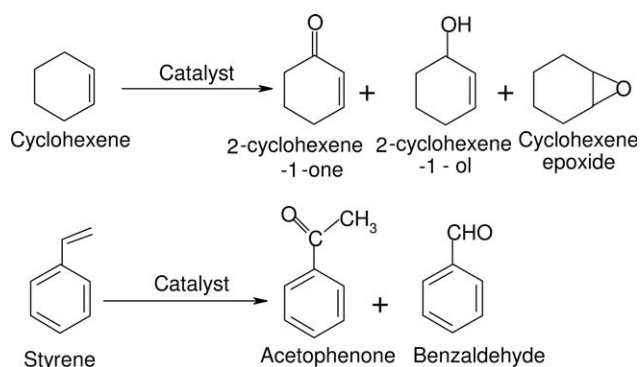
Oxidation of cyclohexene and styrene

Effect of solvent

To optimize the reaction conditions, the effect of different solvent on the conversion of cyclohexene and styrene was investigated using P-[Pd$_2$(seam)$_2$(OAc)$_2$] as a catalyst in the presence of TBHP as oxidant. Acetonitrile (ACN), ethyl acetate (EtOAc), dichloromethane (DCM), methanol (MeOH), tetrahydrofuran (THF), and toluene were used as solvent. The results were shown in Table II. From the results, it is seen that the activity of catalyst was improved with increasing solvent polarity [Polarity Index Value: ACN (5.80), EtOAc (4.4), DCM (3.1), MeOH (5.1), THF (4.0) and toluene (2.4)]. No conversions of cyclohexene and styrene were obtained in nonpolar toluene medium. Acetonitrile, owing to its strong polar and coordination capacity and highest dielectric constant ($\varepsilon/\varepsilon_0 = 35.94$) and dipole moment ($\mu = 3.90$D),[44] is most effective for the present reaction and gave highest conversion and selectivity.

The present catalyst system does not visibly swell in acetonitrile or ethyl acetate. Slight swelling has been observed in the THF medium in which catalytic activity is poor. As all experiments have been performed in acetonitrile medium, swelling is not viewed as a major factor in the present catalyst system.
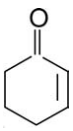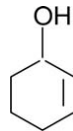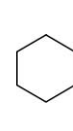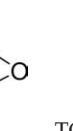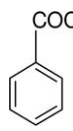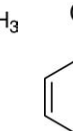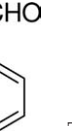
Effect of oxidant

To design the best catalytic system, the ability of different oxidant such as *tert*-butylhydroperoxide (TBHP) (70% aq.), hydrogen peroxide (H$_2$O$_2$) (30% aq.), cumene hydroperoxide, NaOCl, and molecular oxygen was examined in the oxidation of cyclohexene and styrene. As shown in Table II, TBHP in acetonitrile medium is most efficient oxidant source to oxidize cyclohexene and styrene selectively because of unreactiveness in absence of catalyst and good solubility in acetonitrile medium. Use of cumene hydroperoxide, no conversion was obtained. In

Scheme 2 Reaction product on oxidation of cyclohexene and styrene

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TABLE II
Effect of Different Solvents and Oxidants on Oxidation of Cyclohexene and Styrene Catalyzed by
P-[Pd$_2$(seam)$_2$(OAc)$_2$]

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Sl. No.	Solvent	Oxidant	Cyclohexene Conv. (%)	Selectivity (O)	Selectivity (OH)	Selectivity (epoxide)	TOF (h^{-1})	Styrene Conv. (%)	Selectivity (COCH$_3$)	Selectivity (CHO)	TOF (h^{-1})
1.	ACN	TBHP	78	90	8	2	231.18	72	83	17	248.96
2.	MeOH	TBHP	55	87	10	3	163.01	53	81	19	183.26
3.	EtOAc	TBHP	43	79	21	–	127.44	44	75	25	152.14
4.	THF	TBHP	29	84	14	2	85.95	25	77	23	86.44
5.	DCM	TBHP	27	64	32	4	80.02	26	71	29	89.90
6.	Toluene	TBHP	–	–	–	–	–	–	–	–	–
7.	ACN	H$_2$O$_2$	46	81	19	–	136.34	40	64	36	138.31
8.	ACN	NaOCl	38	59	29	12	112.63	29	58	40	100.28
9.	ACN	Mol O$_2$	15	38	22	40	44.46	18	80	20	62.24

Reaction conditions: [substrate] = 5 mmol; catalyst = 40 mg; [oxidant] = 10 mmol; solvent = 10 mL; Temperature = 60°C;

Yield refers to GC & GC-MS analysis.

Turn over frequency (TOF) = moles of substrate converted per mole of Pd per h.

The percentage-conversion of the substrate and the percentage-selectivity of the products in the oxidation reaction are calculated as: Substrate conversion (%) = $\frac{\text{Substrate converted (moles)}}{\text{Substrate used (moles)}} \times 100$, Product selectivity (%) = $\frac{\text{Product formed (moles)}}{\text{Substrate converted (moles)}} \times 100$

presence of molecular oxygen, cyclohexene and styrene was oxidized but lower yield of products were obtained.

Effect of temperature

The effect of temperature on the conversion of styrene and cyclohexene was studied in the temperature range of 30–70°C. At temperatures lower than 30°C, no conversions were observed. As can be seen from Figure 5, the conversion of styrene and cyclohexene gradually increased with an increase in temperature. The maximum conversion of styrene and cyclohexene were observed at 60°C. In contrast, at reaction temperatures above 60°C, a decrease in conversion was observed. This is because at higher temperature, self decomposition of TBHP proceeds faster and it did not participate effectively in the oxidation process.

Effect of reaction time

The effect of reaction time on cyclohexene and styrene oxidation is illustrated in Figure 6. The conversion of cyclohexene and styrene and the selectivity of 2-cyclohexene-1-one and acetophenone using polymer-anchored Pd(II) catalyst have been analyzed as a function of time. As the reaction time increases from 1 h to 7 h, conversion of styrene and cyclohexene increases gradually. Acetophenone selectivity increases with increase of reaction time and

83% selectivity of acetophenone attain after 6 h of reaction, whereas highest selectivity of 2-cyclohexene-1-one (90%) was observed after 7 h.

Effect of amount of catalyst

The amount of catalyst present in the system tremendously affects the over all oxidation efficiency and the selectivity pattern. Three different weights, 0.020, 0.040, and 0.080 g, of catalyst were used to study the
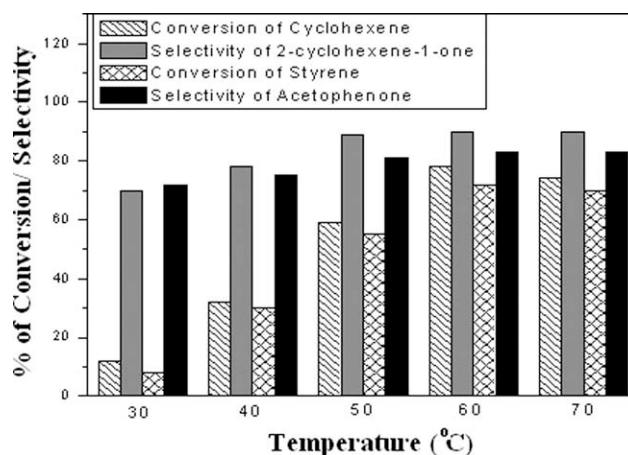

Figure 5 Effect of temperature on the oxidation of cyclohexene and styrene using polymer-anchored Pd(II) complex catalyst. Reaction condition: substrate (5 mmol), acetonitrile (10 mL), TBHP (10 mmol), catalyst (40 mg).
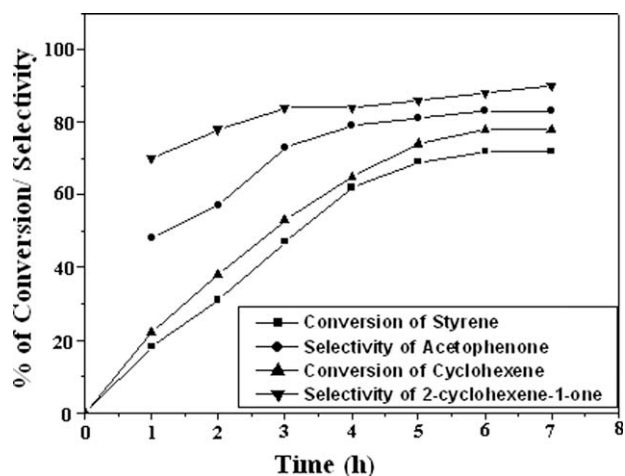
Figure 6 Plot of conversion/selectivity vs. time for oxidation of cyclohexene and styrene using polymer-anchored Pd(II) complex catalyst. Reaction condition: substrate (5 mmol), TBHP (10 mmol), acetonitrile (10 mL), and temperature = 60°C.

influence of the amount of catalyst on conversion of styrene and cyclohexene at 60°C. Results are shown in Figure 7. As seen in the figure, 0.02 g of catalyst gave only a 32% and 37% conversion of styrene and cyclohexene while catalyst loadings of 0.04 g showed maximum conversions of 72% in case of styrene and 78% in case of cyclohexene, respectively, at the end of the 6 h. Further increase in the catalyst amount, no such increment in the yield of product was obtained.

Effect of substrate-to-oxidant ratio

A series of reactions were carried out to establish the effect of substrate-to-oxidant ratio on the conversion and selectivity of cyclohexene and styrene. The results
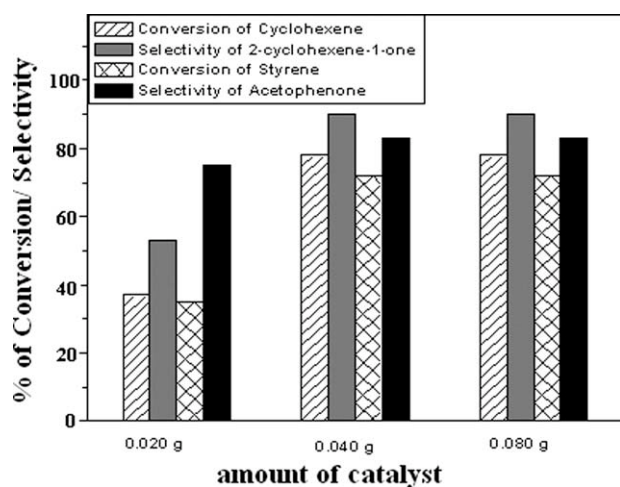

Figure 7 Effect of amount of catalyst on the oxidation of cyclohexene and styrene using polymer-anchored Pd(II) complex catalyst. Reaction condition: substrate (5 mmol), TBHP (10 mmol), acetonitrile (10 mL), and temperature = 60°C.

are presented in Figure 8. Four different molar ratios of substrates to TBHP (e.g., 1 : 0.5, 1 : 1, 1 : 2, and 1 : 3) were used for which 5 mmol of substrates and 40 mg of catalyst were taken in 10 mL of acetonitrile and the reaction was carried out at 60°C. It is observed that as the amount of oxidant increases, the conversion of reactants and the selectivity of products increases. The maximum conversion was observed when two times the oxidant concentration based on substrate was used, while further increment of oxidant concentration shows no further improvement in conversion.

Thus, the required parameters for the oxidation of styrene and cyclohexene were as follows: substrate (5 mmol), TBHP (10 mmol), acetonitrile (10 mL), catalyst (40 mg), temperature 60°C, and reaction time 6 h for styrene and 7 h for cyclohexene, respectively. Styrene was converted to acetophenone with 83% selectivity, whereas cyclohexene was converted to 2-cyclohexene-1-one with 90% selectivity. Blank experiment in the present of oxidant and using the same experimental conditions in absence of catalyst was also carried out for the oxidation of styrene. From the results, it is seen that without catalyst, TBHP has very poor ability to oxidize styrene. Only 12% conversion of styrene takes place after 24 h with 48% selectivity of acetophenone. Thus, the polymer-anchored Pd(II) secondary amine complex not only enhanced the percent conversion of styrene, it also improved product selectivity.

Catalytic oxidation of various olefins and alcohols in presence of polymer-anchored Pd(II) complex catalyst

Oxidation of various olefins and alcohols were performed under the same reaction condition which was optimized for styrene. The results are shown in
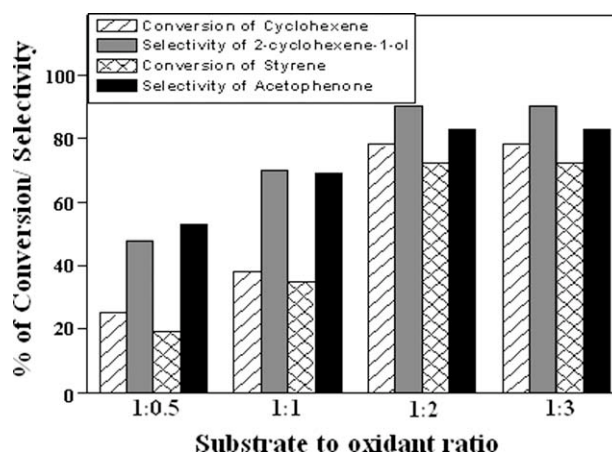

Figure 8 Effect of substrates-to-oxidant molar ratio on the oxidation of cyclohexene and styrene using polymer-anchored Pd(II) complex catalyst. Reaction condition: substrate (5 mmol), TBHP (10 mmol), acetonitrile (10 mL), catalyst (40 mg), and temperature = 60°C.

TABLE III
Catalytic Oxidation of Organic Substrates Using Catalyst P-[Pd$_2$(seam)$_2$(OAc)$_2$]

Entry	Substrate	Product (s)	Conversion	Selectivity	T.O.F (h^{-1})
1.	1-pentene	2-pentanone	63	95	217.84
		3-penten-2-one		5	
2.	1-hexene	2-hexanone	58	100	200.55
3.	1-octene	2-octanone	49	100	169.43
4.	Cyclooctene	2-cyclooctene-1-one	64	87	221.30
		2-cyclooctene-1-ol		13	
5.	Toluene	Benzaldehyde	26	97	89.90
		Benzoic acid		3	
6.	Ethyl benzene	Benzaldehyde	37	70	127.94
		Acetophenone		30	
7.	Benzyl alcohol	Benzaldehyde	80	96	276.63
		Benzoic acid		4	
8.	1-propanol	1-propanal	43	100	148.69
9.	2-propanol	Acetone	39	100	134.85

Reaction conditions: [substrate] = 5 mmol; catalyst = 40 mg; [TBHP] = 10 mmol; acetonitrile = 10 mL; Temperature = 60°C; reaction time 6 h.

Yield refers to GC & GC-MS analysis.

Turn over frequency (TOF) = moles of substrate converted per mole of Pd per h.

Table III. Pentene was oxidized to 2-pentanone and 3-penten-2-one with some other unidentified polymeric tarry materials. 1-hexene, 1-octene were oxidized to corresponding 2-one. Toluene was oxidized mainly to benzaldehyde with benzoic acid as minor product. The formation of benzoic acid in reaction mixture was detected only after the accumulation of substantial amount of benzaldehyde in the reaction mixture. Alkan-1-ol was oxidized to the corresponding aldehyde, whereas alkan-2-ol was found to oxidized to ketone. Benzaldehyde was the oxidized product of benzyl alcohol.

With P-[Pd$_2$(seam)$_2$(OAc)$_2$] as catalyst, the substrates may be arranged in the following order in accordance to their initial rate of oxidation:

Benzyl alcohol > styrene > cyclohexene > cyclooctene > 1-pentene > 1-hexene > 1-octene > 1-propanol > 2-propanol > ethylbenzene > toluene

From the rate of oxidation of substrates (Table III), it appeared that the double bond which is a part of a delocalized system was oxidized more quickly than the localized one. Styrene was found to oxidize more quickly than the cyclohexene and 1-hexene. In case of terminal olefins, the rate of oxidation was decreased with increase of molecular weight of alkenes. Comparative poor mobility of terminal olefins having higher molecular weight might be the reason for their slow rate of oxidation. Same observation was observed in case of alcohol also. Because of the presence of greater steric hindrance, 2-propanol was found to oxidize much more slowly than that of respective 1-propanol. Lower conversion of toluene and ethyl benzene may be due to difficulty in direct functionalization of the unactivated C—H bond under present reaction conditions.

Comparison of catalytic activities of polymer-anchored metal complexes with its homogeneous analogue

To see the effect of anchoring, oxidation of styrene, cyclohexene, and benzyl alcohol were conducted in presence of catalysts P-[Pd$_2$(seam)$_2$(OAc)$_2$] and the corresponding homogeneous complex [Pd$_2$(seam)$_2$ (OAc)$_2$] and the results are presented in Table IV. From our experimental results, it seems that present heterogeneous palladium catalyst can perform almost equally well as homogeneous one. Additionally, the supported catalyst is expected to have several advantages over the homogenous one. The polymer-based catalysts can withstand more drastic conditions, easily recovered from the reaction mixture, and can influence product distribution due to their steric factors. Oxidation of benzyl alcohol with polymer-anchored catalyst give benzaldehyde with 96% selectivity, whereas we get 62% selectivity of benzaldehyde with homogeneous catalyst. The disadvantage of homogeneous palladium complex is the catalyst degradation, whereas the heterogenized palladium complex can be reused several times without significant loss of its activity. Finally, from the obtained results, it is seen that the reaction times are slightly longer in the heterogeneous system than the homogeneous system.

Heterogeneity tests

An important criteria in the commercial applications of Pd catalyst is to obtain palladium free end

TABLE IV
Oxidation of Olefins with TBHP Catalyzed by [Pd$_2$(seam)$_2$(OAc)$_2$] and P-[Pd$_2$(seam)$_2$(OAc)$_2$]

Entry	Substrate	Product (s)	Homogeneous [Pd$_2$(seam)$_2$(OAc)$_2$]			Heterogeneous P-[Pd$_2$(seam)$_2$(OAc)$_2$]		
			Time	Conversion (%)	Selectivity (%)	Time	Conversion (%)	Selectivity (%)
1.	Styrene	Acetophenone	5	70	55	6	72	83
		Benzaldehyde			45			17
2.	Cyclohexene	2-cyclohexene-1-one	5	78	67	7	78	90
		2-cyclohexene-1-ol			21			8
		Cyclohexene epoxide			12			2
3.	Benzylalcohol	Benzaldehyde	5	81	62	6	80	96
		Benzoic acid			38			4

Reaction conditions: [substrate] = 5 mmol; catalyst = 40 mg; [TBHP] = 10 mmol; acetonitrile = 10 ml; Temperature = 60°C.

Yield refers to GC & GC-MS analysis.

Turn over frequency (TOF) = moles of substrate converted per mole of Pd per h.

products, as metal contamination is of great concern for food and pharmaceutical industries and to lose small amounts of the expensive Pd catalyst. To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test[45] was performed in the oxidation reaction of styrene. During catalytic reaction, the solid catalyst was separated from the reaction mixture by filtration after 3 h and the determined conversion was 47%. The reaction was carried out for a further 2 h. The gas chromatographic analysis showed no increment in the conversion. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirms that Pd is absent in the reaction mixture. These results suggest that the Pd is not being leached out from the catalyst during catalytic reactions.

Recycling of the catalyst

An advantage of the polymer-anchored catalyst is that the catalyst can be easily synthesized, do not need any complicated equipments, it can withstand more stringent reaction conditions, can be removed easily from the reaction mixture, and more easily handled. The reusability of P-[Pd$_2$(seam)$_2$(OAc)$_2$] for oxidation of styrene has been studied and the results are given in Figure 9. After completion of reaction, the solid catalyst was separated from the liquid reaction mixture by simple filtration, followed by several washings with acetonitrile and methanol. After filtration, the recovered catalyst dried under vacuum and then used in the oxidation processes with a fresh reaction mixture. The catalyst could be almost recovered and recovered catalyst showed almost the same catalytic activity as the first time. After the seventh catalyst reuse, the selectivity of acetophenone was close to 80% in all cases, and the conversion was decreased by 4%.

CONCLUSIONS

A polymer-anchored secondary amine palladium complex P-[Pd$_2$(seam)$_2$(OAc)$_2$] (seam = secondary amine) has been synthesized and characterized. This immobilized palladium catalyst was used in the liquid phase oxidation of olefins and alcohols where it showed excellent catalytic activity in the presence of *tert*-butylhydroperoxide as an oxidant. Experimental results shown above suggested that the functionalization of the polymeric surface with Pd(II) complex is very efficient for designing an eco-friendly catalyst exhibiting significant catalytic activity with higher yields. The remarkable advantages with the use of the catalyst are the easy preparation, handling stability, and moisture insensitivity. Easily recoverable and reusability makes the catalyst highly cost effective and environmentally acceptable. The catalysts can be easily separated from the reaction mixture by simple filtration and reused after washing without significant degradation in catalytic activity.
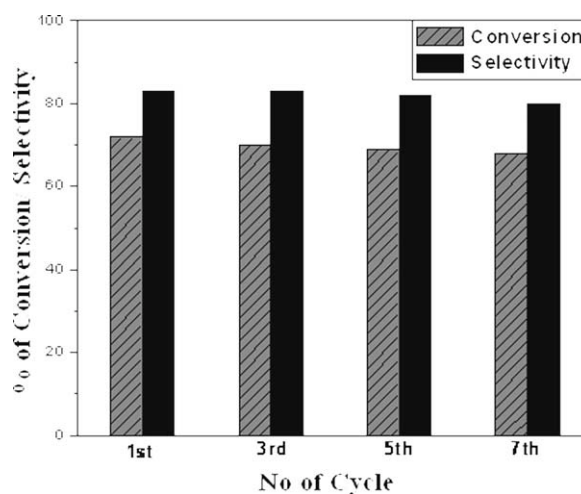

Figure 9 Recycling efficiency of polymer-anchored Pd(II) complex catalyst for the oxidation of styrene.

References

1. Parshall, G. W. Homogeneous Catalysis: The Application of Catalysis by Soluble Transition Metal Complexes; Wiley: New York, 1980.
2. Sheldon, R. A.; Kochi J. K. Metal-Catalyzed Oxidations of Organic Compounds; Academic Press: New York, 1981.
3. Meunier, B. Chem Rev 1992, 92, 1411.
4. Garrett, C. E.; Prasad., K. Adv Synth Catal 2004, 346, 889.
5. Jahnisch, K.; Hessel, V.; Lowe, H.; Baerns, M. Angew Chem Int Ed 2004, 43, 406.
6. Hill, C. L. Angew Chem Int Ed 2004, 43, 402.
7. Stahl, S. S. Angew Chem Int Ed 2004, 43, 3400.
8. Sigman, M. S.; Schultz, M. J. Org Biomol Chem 2004, 2, 2551.
9. Jorgenson, K. A. Chem Rev 1989, 89, 431.
10. Zimowska, M.; Michalik-Zym, A.; Poltowicz, J.; Bazarnik, M.; Bahranowski, K.; Serwicka, E. M. Catal Today 2007, 124, 55.
11. Samanta, S.; Mal, N. K.; Bhaumik, A. J Mol Catal A Chem 2005, 236, 7.
12. Mukherjee, S.; Samanta, S.; Roy, B. C.; Bhaumik, A. Appl Catal A Gen 2006, 301, 79.
13. Van Der Vlugt, J. I.; Meyer, F. Top Organomet Chem 2007, 22, 191.
14. Welch, C. J.; Albaneze-Walker, J.; Leonard, W. R.; Biba, M.; Dasilva, J.; Henderson, D.; Laing, B.; Mathre, D. J.; Spencer, S.; Bu, X.; Wang, T. Org Process Res Dev 2005, 9, 198.
15. Li, F.; Zhang, Q.; Wang, Y. Appl Catal A Gen 2008, 334, 217.
16. Jin, C.; Fan, W.; Jia, Y.; Fan, B.; Ma, J.; Li, R. J Mol Catal A: Chem 2006, 249, 23.
17. Skoglundh, M.; Löwendahl, L. O.; Otterated, J.-E. Appl Catal 1991, 77, 9.
18. Serwicka, E. M.; Połtowicz, J.; Bahranowski, K.; Olejniczak, Z.; Jones, W. Appl Catal A Gen 2004, 275, 9.
19. Hou, Z.; Theyssen, N.; Brinkmann, A.; Klementiev, K. V.; Grünert, W.; Bühl, M.; Schmidt, W.; Spliethoff, B.; Tesche, B.; Weidenthaler, C.; Leitner, W. J Catal 2008, 258, 315.
20. Mukherjee, S.; Samanta, S.; Bhaumik, A.; Roy, B. C. Appl Catal B Environ 2006, 68, 12.
21. Bussi, J.; López, A.; Peña, F.; Timbal, P.; Paz, D.; Lorenzo, D.; Dellacasa, E. Appl Catal A Gen 2003, 253, 177.
22. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Shams, E.; Rasouli, N. Appl Catal A Gen 2008, 334, 106.
23. Gupta, K. C.; Sutar, A. K. J Mol Catal A: Chem 2008, 280, 173.
24. Valodkar, V. B.; Tembe, G. L.; Ravindranathan, M.; Ram, R. N.; Rama, H. S. J Mol Catal A: Chem 2004, 208, 21.
25. Zahalka, H. A.; Januszkiewicz, K.; Alper, H. J Mol Catal 1986, 35, 249.
26. Li, X.; Geng, W.; Wang, F.; Wang, L. Chin J Catal 2006, 27, 943.
27. Bueno, A. C.; De Souza, Á. O.; Gusevskaya, E. V. Adv Synth Catal 2009, 351, 2491.
28. Paavola, S.; Zetterberg, K.; Privalov, T.; Csöregh, I.; Moberg, C. Adv Synth Catal 2004, 346, 237.
29. Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. J Org Chem 1999, 64, 6750.
30. Schultz, M. J.; Park, C. C.; Sigman, M. S. Chem Commun 2002, 3034.
31. Ulmann, S. Encyclopedia of Industrial Chemistry, 6th ed.; Wiley/VCH: New York/Weinheim, 1998.
32. Neumann, R.; Dahan., M. Nature 1997, 388, 353.
33. Lingaiah, N.; Reddy, K. M.; Babu, N. S.; Rao, K. N.; Suryanarayana, I.; Prasad, P. S. S. Catal Commun 2006, 7, 245.
34. Cooke, P. R.; Lindsay Smith, J. R. J Chem Soc Perkin Trans 1913, 1994.
35. Vogel, A. I. Text Book of Practical Organic Chemistry, (Quantitative analysis), 5th ed.; Longman: London, 1989.
36. King, R. B.; Sweet, E. M. J Org Chem 1979, 44, 385.
37. Velluz, L.; Amiard, G.; Heymes, R. Bull Sot Chim Fr 1954, 1012.
38. Teranishi, T.; Toshima, N. J Chem Soc Dalton Trans 1994, 2967.
39. Dalal, M. K.; Ram, R. N. J Mol Catal A: Chem 2000, 159, 285.
40. Onoue, H.; Moritani, I. J Organomet Chem 1972, 43, 431.
41. Lever, A. B. P. Inorganic Electronic Spectroscopy, 1st ed.; Elsevier: Amsterdam, 1968.
42. Mostafa, S.; Perlepes, S. P.; Hadjiliadis, N. Z Naturforsch 2001, 56, 394.
43. Sarkar, S.; Dey, K. Spectrochim Acta A 2005, 62, 383.
44. Monfared, H. H.; Sadighian, S.; Kamyabi, M. A.; Mayer, P. J Mol Catal A: Chem 2009, 304, 139.
45. Niasari, M. S.; Kabutarkhani, M. H.; Davar, F. Catal Commun 2006, 7, 955.