Polymer-Supported Palladium(II) Complexes and Their Catalytic Study

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ABSTRACT: Chloromethylated poly(styrene–divinylbenzene) copolymers with 8 and 14% crosslinking was functionalized to a Schiff-base-bearing polymer by the sequential oxidation of the chloromethyl group to an aldehydic group and subsequent condensation with a base. The anchoring of the metal ion to the liganded polymer beads was carried out by its reaction with an ethanolic solution of palladium(II) chloride. The physicochemical properties of the supported catalyst, including surface area, bulk density, and the swelling of the polymer in polar and nonpolar solvents, were studied. The catalysts were characterized by various techniques, including elemental analysis, DTA–thermogravimetric analysis, Fourier transform infrared spectroscopy, and diffuse reflectance spectroscopy. The surface morphology of the catalyst was studied by scanning electron microscopy. The catalytic hydrogenation of *cis*-cyclooctene was investigated with the immobilized catalysts. The effects of various reaction parameters, including catalyst concentration, temperature, and hydrogen pressure on the reduction of olefin, were studied. The rate of the reaction was determined from hydrogen uptake measurements. © 2003 Wiley Periodicals, Inc.
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INTRODUCTION

The immobilization of metal complexes on a polymer matrix is a useful method of heterogenizing a homogeneous catalyst.[1–3] Polymer-bound metal complexes can offer the combined advantages of homogeneous (mild reaction conditions) and heterogeneous (easy separation) catalysts. A number of studies have been made while supporting the metal complex on inorganic supports or on a polymer.[4,5] One promising approaches for anchoring palladium complexes is the chelation of molecules such as diphosphine[6] and Schiff bases.[7] This is because palladium is known to form stable complexes with a wide variety of organic ligands with P, N, and O atoms. Moreover, the functional tolerance of these Pd complexes is quite good.[7] A few Schiff bases have been anchored to the polystyrene matrix because of their pronounced coordinating properties.[8,9] An attempt has been made in this study to synthesize Pd(II) complexes with polymeric Schiff bases derived from ethylenediamine and 2-aminopyridine and to investigate their catalytic activity in the hydrogenation of *cis*-cyclooctene.

EXPERIMENTAL

Materials

Chloromethylated poly(styrene–divinylbenzene) [P(S–DVB)] as spherical beads with 8 and 14% crosslinking

[18–44 mesh, chlorine content = 14 and 22%, respectively] were received from Ion Exchange India Ltd. (Mumbai, India). We estimated the chlorine content in the beads gravimetrically to ascertain the extent of chloromethylation.[1] 2-Aminopyridine (Merck, Germany), ethylenediamine (Ranbaxy, India), and palladium(II) chloride (Loba Chemie, India) were used as received. 1,4-Dioxane, methanol, and ethanol (Analytical Reagent (AR) grade) were purified by standard methods.[10]

### Preparation of P(S–DVB)-supported palladium(II)/Schiff-base complexes

Conversion of the chloromethyl group to an aldehydic function

In a typical experiment, chloromethylated P(S–SB) copolymer beads (20 g, 8 or 14% crosslinking) were stirred in dimethyl sulfoxide (DMSO; 170 mL) with sodium bicarbonate (10 g) for 6 h at 155°C.[11] The beads were collected on a glass filtration funnel; washed with DMSO, hot water, and mixture of dioxane and water (2:1 v/v) in that sequence; and rinsed with ethanol and finally with benzene. About 19 g of cream-colored aldehyde functionalized beads were obtained after the beads were dried at 100°C for 24 h *in vacuo*. The functionalized copolymer beads were used for the synthesis of the Schiff-base ligand on the polymer.

Preparation of Schiff-base-functionalized P(S–DVB) copolymers

The polymer beads (10 g) bearing the —CHO group were allowed to swell in methanol (50 mL) for 1 h. To
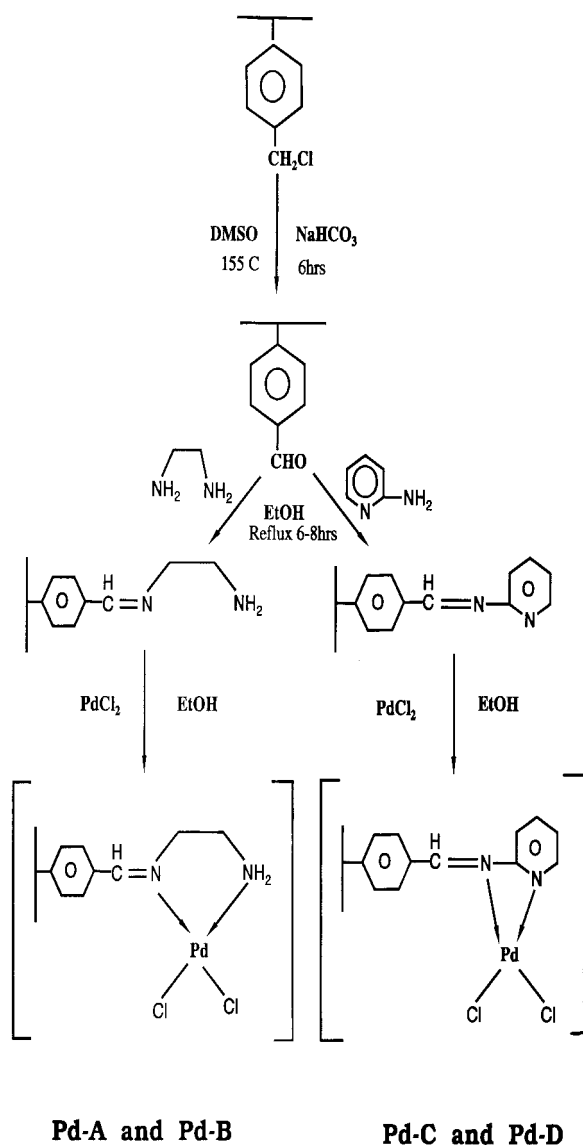
Scheme 1 Synthesis of polymer-supported Pd(II)/Schiff-base complexes.

TABLE II
Physicochemical Properties of the Catalysts

Property	Pd-A	Pd-B	Pd-C	Pd-D
Surface area (m^2g^{-1})	32	34	31	31
Pore volume (cm^3g^{-1})	0.206	0.207	0.191	0.203
Apparent bulk density ($gm\ cc^{-1}$)	0.460	0.465	0.450	0.445
Moisture content (%)	1.5	1.4	1.0	0.9

this, a solution of ethylenediamine (0.5 mol in 25 mL of methanol) was added dropwise over a period of 45 min with constant stirring. The contents were refluxed for 8 h. After they were cooled to room temperature, the pale yellow colored polymer beads were filtered, washed thoroughly with methanol and petroleum ether (40–60°C), and dried *in vacuo* at 70°C for 24 h. The Schiff base with 2-aminopyridine was similarly prepared with 0.24 mol of the amine in place of ethylenediamine.

Incorporation of palladium onto a Schiff-base-bearing resin

The Schiff-base-bearing polymer beads (10 g) were allowed to swell in ethanol (50 mL) for 45 min. To this, 5 mmol of PdCl₂ in ethanol (50 mL) was added over a period of 45 min with occasional shaking. The contents were initially heated to 50°C for 6 h and then cooled and agitated on a shaker for 2 weeks at room temperature. At the end of this period, the color of the beads changed to intense yellow, indicating the formation of a palladium complex on the surface of the polymer. The beads were filtered, carefully washed with ethanol, and finally dried *in vacuo* at 70°C for 24 h.

Hydrogenation of *cis*-cyclooctene

The kinetics of the hydrogenation of *cis*-cyclooctene in methanol was studied at atmospheric pressure by the

TABLE I
Elemental Analysis of Catalysts at Various Stages of Preparation

Compound	C %	H %	N %	Pd (mmole g^{-1} of resin)
8% P(S–DVB)–CH₂Cl	67.62	5.67	—	—
14% P(S–DVB)–CH₂Cl	81.79	7.03	—	—
8% P(S–DVB)–CHO	81.36	7.03	—	—
14% P(S–DVB)–CHO	86.20	7.49	—	—
8% P(S–DVB) (en-SB)	76.55	7.08	2.03	—
14% P(S–DVB) (en-SB)	85.56	7.63	1.66	—
8% P(S–DVB) (2ap-SB)	75.76	6.61	1.10	—
14% P(S–DVB) (2ap-SB)	84.65	7.36	1.05	—
Pd-A	71.85	6.62	1.62	4.32×10^{-5}
Pd-B	82.46	7.48	1.44	2.76×10^{-5}
Pd-C	75.56	6.50	0.97	4.78×10^{-5}
Pd-D	84.35	7.28	0.86	3.03×10^{-5}

TABLE III
Swelling Behaviour of the Catalysts at 25°C (mole%)

Solvent	Pd-A	Pd-B	Pd-C	Pd-D
Water	4.3	5.2	4.9	5.6
Methanol	2.6	2.9	2.7	2.9
Ethanol	1.8	2.0	2.0	2.2
Acetonitrile	2.0	2.3	2.2	2.4
Benzene	1.3	1.2	1.2	1.2
Tetrahydrofuran	1.1	1.2	1.2	1.3
n-Heptane	0.9	0.9	0.9	1.0

measurement of the hydrogen uptake at different intervals of time in a magnetically stirred three-necked glass reactor after a procedure described earlier.[12,13] The influence of temperature, substrate, and catalyst concentration on the progress of the reaction was studied.

The effect of hydrogen pressure (20–40 psig H_2) on the hydrogenation of *cis*-cyclooctene was studied at room temperature in a 500-mL shaker-type stainless steel Parr hydrogenator, into which were charged catalyst (100 mg); the substrate *cis*-cyclooctene (10 mmol); and methanol (20 mL). The reaction vessel was connected to a hydrogen reservoir with a pressure gauge from which the required hydrogen pressure was supplied. The progress of the reaction was followed by observation of the drop in hydrogen pressure. After 24 h, the reaction was stopped and bottle depressurized, and the contents were carefully separated from the catalyst by filtration. The filtrate was analyzed by gas chromotography with chlorobenzene as an internal standard. The high-pressure hydrogenation reactions of *cis*-cyclooctene at 50°C were carried out with a 160-mL Parr reactor (USA) connected to a model 4842 PID controller.

Analysis

Elemental analyses of polymer-supported metal complexes were carried out with a Carlo Erba Strumentazione microanalyzer (Italy). Palladium content in the polymer-supported complexes was estimated by digestion of the catalyst (0.2 g) with concentrated HNO_3 (10 mL). The analyte was diluted to 50 mL in a volumetric flask and analyzed on GBC 902 AAS instrument (Australia). Thermal analysis of the support and the catalysts were carried out in a N_2 atmosphere on a TA Instruments 2950 thermal analyzer (USA) at a heating rate of 10°C min^{-1}. Scanning electron microscopy was performed on a Jeol JSM-T300 instrument (Japan). IR and far-IR spectra were recorded on a Nicolet Magna 550 spectrophotometer (4000 to 50 cm^{-1}) (USA). Diffuse reflectance spectra (200–500 nm) were recorded on a Shimadzu UV-240 instrument (Japan) with $BaSO_4$ as the nonabsorbing standard. GC analysis of the hydrogenation products were carried out on a Shimadzu 15A gas chromatograph on a 15% Carbowax column (stainless steel (SS), 1/8 in. × 2 m) with a flame ionization detector. Nitrogen was used as a carrier gas with a flow rate of 30 mL min^{-1}. The surface area of the support and the catalysts were determined on a Carlo Erba surface analyzer with the Brunauer–Emmett–Teller relationship. The swelling behavior of the polymer-supported catalysts in polar and nonpolar solvents was studied at 27 ± 1°C.

RESULTS AND DISCUSSION

The functionalization of the chloromethylated P(S–DVB) with a Schiff-base ligand and the loading of palladium metal to form the polymer-supported Pd/Schiff-base complex was carried out as shown in Scheme 1. The catalysts employed in the study were

TABLE IV
IR Frequencies (cm^{-1}) of poly(benzene) Supported Schiff Base and Their Palladium Complexes

Compound	νNH	νC=N	Py ring	Py ring N + νC=N stretch	νPd—Cl	νPd—N
8% P(S-DVB) (en-SB)	3410 br	1646 s				
14% P (S-DVB) (en-SB)	3430 br	1646 s				
8% P(S-DVB) (2ap-SB)		1669 s	1606 ms 1568 ms	777 ms		
14% P(S-DVB) (2ap-SB)		1669 s	1606 ms 1568 ms	764 ms		
Pd-A	3406 br	1613 s			310 w	480 w 525 w
Pd-B	3423 br	1626 s			359 w	466 w 543 w
Pd-C		1649 s	1600 ms 1513 ms	758 ms	355 w	485 w 521 w
Pd-D		1649 s	1600 ms 1513 ms	754 ms	362 w	467 w 543 w

^{a} br = broad; ms = medium strong; s = strong; w = weak.

designated as Pd-A [8% P(S–DVB) Pd(II) (en-SB)], Pd-B [14% P(S–DVB) Pd(II) (en-SB)], Pd-C [8% P(S–DVB) Pd(II) (2ap-SB)], and Pd-D [14% P(S–DVB) Pd(II) (2ap-SB)].

Catalyst characterization

Microanalyses of Pd-A to Pd-D at different stages of preparation are presented in Table I. The physical properties of the synthesized catalysts are shown in Table II. From Table I, one can infer that the nitrogen content in the Pd-A and Pd-C was higher than in Pd-B and Pd-D, which was attributed to the difference in the degree of crosslinking of the supports. Moreover, less functionalization was observed in Pd-B and Pd-D. This behavior is expected in the case of supports with higher degrees of crosslinking because the polymer networks consist of dense and inaccessible domains leading to less functionalization.[14] A decrease in surface area in all of the catalysts was observed (Table II) on loading the metal on to the functionalized polymer support. This indicates partial blocking of pores of the functionalized polymer support on complexation.[15] Pd-A and Pd-B had slightly higher surface areas (32.7 and 34.2 m^2 g^{-1}) than Pd-C and Pd-D (31.1 and 31.2 m^2 g^{-1}), which could be ascribed to the relative size differences in the Schiff base derived from ethylenediamine and 2-amino-pyridine.[16] The swelling behavior of the catalysts in polar and nonpolar solvents was studied (Table III). Water, methanol, and acetonitrile showed higher swelling percentages. However, for practical purposes, methanol was used as the solvent of choice because it exhibited better properties for the dissolution of the substrate olefin.

The mid-IR (4000–400 cm^{-1}) and far IR (400–50 cm^{-1}) spectra of catalysts at different stages of preparation were recorded, and the IR frequencies are compiled in Table IV.

As shown in the IR data, the C═N (azomethine) band in the 1660-cm^{-1} region in Schiff-base-liganded polymer shifted to lower values (1646–1613 cm^{-1}) on complexation with palladium, indicating N coordination of the ligand to the metal ion. Further, the complexation of the ethylenediamine Schiff base to Pd(II) was indicated by a marginal low-frequency shift in the νNH band (~3400 cm^{-1}) for Pd-A and Pd-B. Similarly, the coordination of the 2-aminopyridine Schiff base to Pd(II) in Pd-C and Pd-D was confirmed by a shift to lower values (from 1606 to 1600 cm^{-1} and 1568 to 1513 cm^{-1}) in the pyridine ring frequencies on complexation.[17] Further, in the far-IR spectra of the polymer-supported Pd complexes, two new low intensity bands in the regions 360–310 cm^{-1} and 485–460 cm^{-1} were observed. These were assigned to Pd–Cl and Pd–N vibrations.

The ultraviolet–visible reflectance spectra of the catalysts are shown in Figure 1. Because of low metal
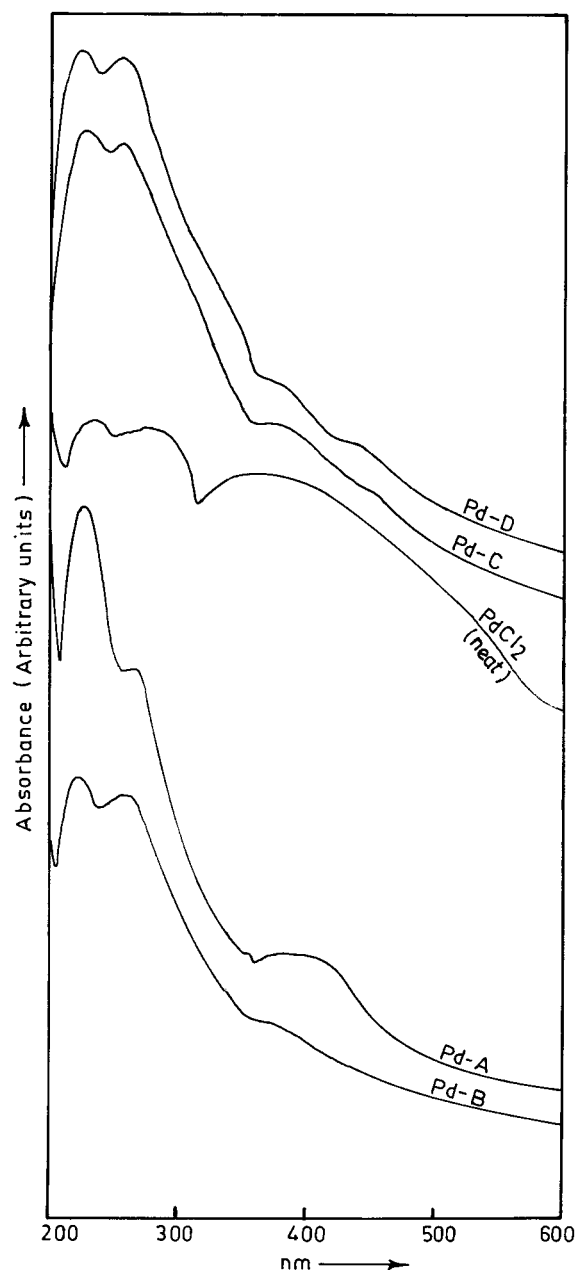

Figure 1 Diffuse reflectance spectra of the catalysts.

loading (~10^{-5} mol g^{-1} of resin), the intensities of the bands were affected. Low-intensity bands at 240 and 320 nm were observed for all of our catalysts, which were assigned to $Pd^{+2} \rightarrow N$ coordination.[18,19] Ligand-to-metal charge-transfer bands were not seen in this region.

We recorded scanning electron micrographs of the catalysts to understand the morphological changes occurring on the surface of the polymer matrix. A fine dispersion of palladium was noticed on the smooth spherical surface of the support at a resolution of $10^4\times$ (magnification). Accurate analysis of morphological changes on the surface of the polymer matrix was not possible due to very low loading of metal on the
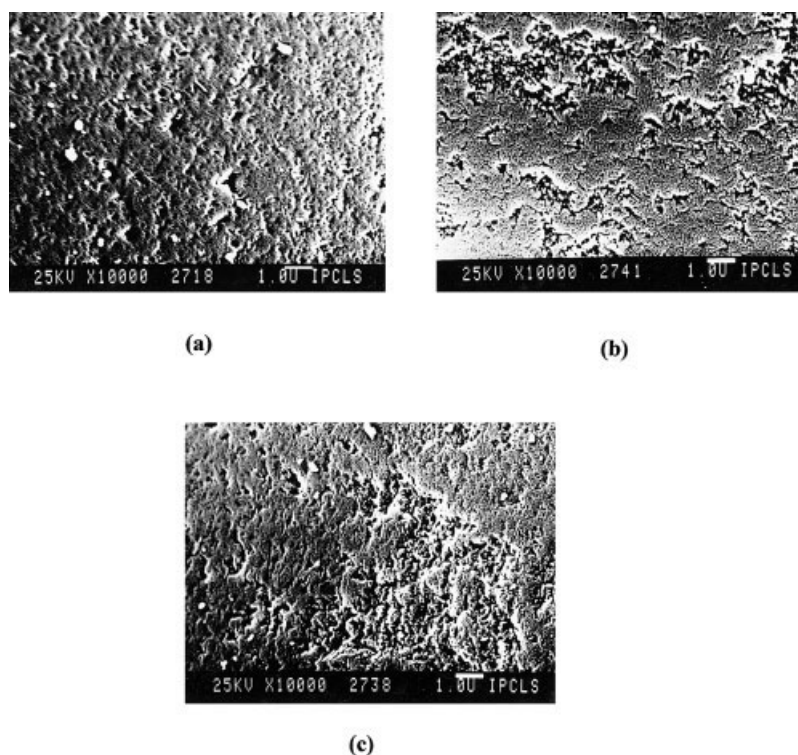
Figure 2   Representative scanning electron micrographs: (a) Pd-A, (b) Pd-B, and (c) Pd-C.

support. The representative micrographs are shown in Figure 2.

Thermogravimetric analysis (TGA) of the Pd-supported catalysts indicated degradation in the 400–450°C temperature range (Table V). An increase in the thermal stability of the polymer-supported catalysts with increasing crosslinking was observed. The degradation of unsupported polymers at lower temperatures with higher weight loss was observed compared to supported Pd complexes, which may have been due to partial dissociation of the Schiff-base ligand moiety from the surface of the polymer.

Hydrogenation of *cis*-cyclooctene

The kinetics of *cis*-cyclooctene hydrogenation were investigated for Pd-A to Pd-D. The data on the hydro-

genation reactions were obtained by measurement of the hydrogen uptake at different intervals of time. The rate of hydrogenation was calculated from the slope of the plot of volume of H_2 absorbed (STP) as a function of time. A representative plot is shown in Figure 3. The results are presented in Tables VI–IX. The effect of various reaction parameters on the rate was also studied.

Effect of substrate concentration

The influence of cyclooctene concentration on the rate of hydrogenation was determined at constant palladium concentrations of 4.32×10^{-6} mol for Pd-A, 2.76×10^{-6} mol for Pd-B, 4.98×10^{-6} mol for Pd-C, and 3.03×10^{-6} mol for Pd-D at 30°C. The rate of reaction increased with increasing substrate concentration.[20,21] The rate of hydrogenation was slightly higher for Pd-B and Pd-D than for Pd-A and Pd-C. The order of reaction calculated from the slope of the linear plots of the logarithm of the initial rate versus the logarithm of the substrate was of fractional order with respect to the substrate.[22]

Effect of catalyst concentration

The variation of catalyst concentration on the rate of hydrogenation was investigated at a constant temperature. As expected, the rate of hydrogenation increased with catalyst concentration but reached an

TABLE V
TGA of Polymer Supported Schiff Bases and Catalysts

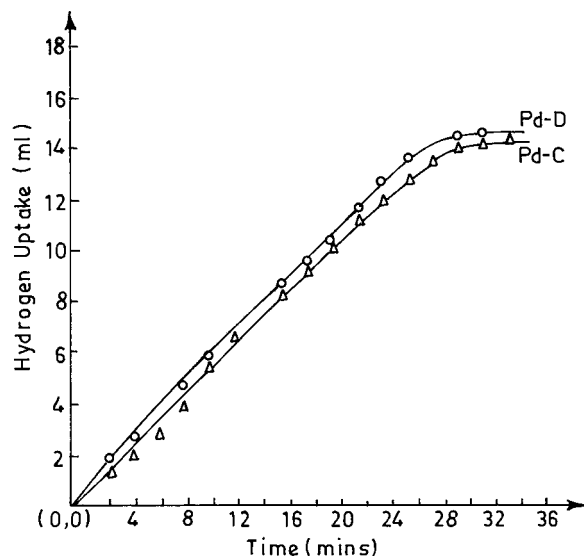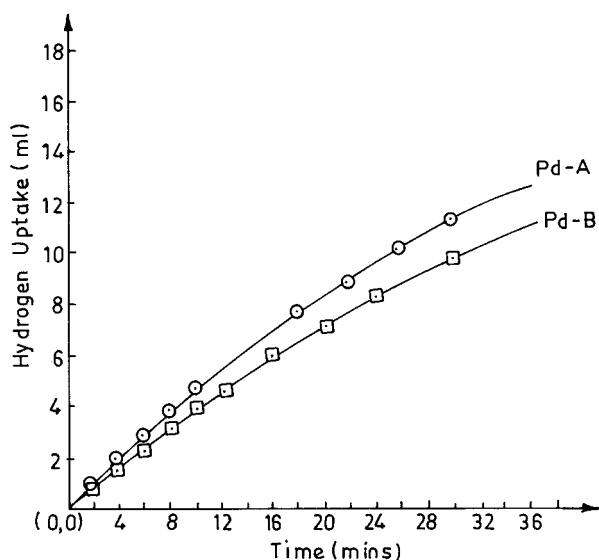| Compound	Degradation-temperature (°C)	Weight loss (%)
8% P(S-DVB) (en-SB)	412.9	47.2
14% P(S-DVB) (en-SB)	394.4	61.1
8% P(S-DVB) (2ap-SB)	378.9	32.7
14% P(S-DVB) (2ap-SB)	408.9	73.8
Pd-A	421.6	41.3
Pd-B	437.5	50.2
Pd-C	425.6	37.3
Pd-D	442.1	46.0

Figure 3 Time versus hydrogen uptake of the Pd catalysts in the hydrogenation of *cis*-cyclooctene.

optimum level after about 30–45 min, which may have been due to the nonavailability of an optimum number of active sites at this concentration.[22] The order of reaction was again found to be of fractional order.

Effect of temperature

The effect of temperature on the rate of hydrogenation was studied in the range 25–40°C with a fixed catalyst and substrate concentration. The initial rate of hydrogenation was found to increase with increasing temperature for all of the catalysts. The activation energy (E_a) was calculated from the slope of the Arrhenius plots (Fig. 4) and was found to be 11.3 kcal/mol (Pd-A), 5.78 kcal/mol (Pd-B), 9.79 kcal/mol (Pd-C) and

7.19 kcal/mol for Pd-D. E_a for the reaction was low compared to the high bond-dissociation energy of the hydrogen molecule.[23,24] One possible reason for this observation may have been the formation of an intermediate complex with a Pd metal center, which could provide an alternate low-energy path for the reaction.

Effect of hydrogen pressure

The influence of hydrogen pressure on the conversion of *cis*-cyclooctene to cyclooctane was studied at room temperature (20–40 psi H_2) and at 50°C (200–400 psi H_2). The results are compiled in Tables VIII and IX. The conversion of *cis*-cyclooctene to cyclooctane was found to increase with increasing hydrogen pressure. Kinetic experiments revealed that the initial rate of hydrogenation varied linearly with hydrogen pressure.[25]

Catalyst recycling

One of the main objectives of supporting a homogeneous metal complex onto a polymeric support is to evaluate the potential of the catalyst for reuse in continuous runs. A preliminary study of the recycling efficiency of Pd-A and Pd-C was carried out on the hydrogenation of *cis*-cyclooctene. The reactions were performed at 27°C in a SS shaker-type Parr reactor (500 mL), into which were charged catalyst (100 mg), *cis*-cyclooctene (1.1 mL, 10 mmol), and methanol (20 mL). The reactor was pressurized to 40 psig H_2 and agitated for 24 h. At the end of this period, the vessel was depressurized, and the catalyst beads were carefully separated from the reaction mixture containing the products and dried to constant weight *in vacuo*. The same material was reused in subsequent cycles. The filtrate containing the product was analyzed by gas chromatography after each cycle. These results are summarized in Table X. It is evident from the data in Table X that even after six cycles, both Pd-A and Pd-C continued to exhibit residual activity. The cyclooctane yields were lowered by about 20% for Pd-A and about 31% for Pd-C. The activity of these catalysts under flow conditions is currently being examined.

CONCLUSIONS

With a simple synthetic sequence, P(S–DVB) beads were chemically modified into bidentate Schiff-base-bearing ligands. The complexation of Palladium with these ligands led to efficient hydrogenation catalysts. Higher temperatures and pressure of H_2 favored better olefin conversions. A proper understanding of the effects of degree of crosslinking in the virgin polymer will help in designing Pd catalysts with enhanced activity for the hydrogenation of unsaturated compounds.

TABLE VI
Summary of the Kinetics of the Hydrogenation of *cis*-Cyclooctene for Pd-A and Pd-B

Catalyst	Pd content ($\times 10^{-6}$ mole)	*cis*- Cyclooctene ($\times 10^{-4}$ mole)	Temperature (°C)	Rate of reaction (mL/min)	E_a (kcal/mole)
Pd-A	2.16			0.37	
	4.32	1.53	30	0.42	
	6.48			0.49	
	8.64			0.53	
	4.32	0.90	30	0.32	
		2.30		0.49	
		3.63		0.57	
	4.32	1.53	25	0.33	
			35	0.43	11.31
			40	0.47	
Pd-B	1.38			0.36	
	2.76	1.53	30	0.47	
	4.14			0.51	
	5.52			0.64	
	2.76	0.90	30	0.33	
		2.30		0.51	
		3.63		0.63	
	2.76	1.53	25	0.35	
			35	0.50	5.78
			40	0.67	

[a] Reaction conditions: solvent = 20 mL of methanol; pH$_2$ pressure = 1 atm.

TABLE VII
Summary of the Kinetics of the Hydrogenation of *cis*-Cyclooctene for Pd-C and Pd-D

Catalyst	Pd content ($\times 10^{-6}$ mole)	*cis*-Cyclooctene ($\times 10^{-4}$ mole)	Temperature (°C)	Rate of reaction (mL/min)	E_a (kcal/mole)
Pd-C	2.39			0.28	
	4.78	1.53	30	0.38	
	7.17			0.46	
	9.56			0.56	
	4.78	0.90	30	0.28	
		2.30		0.52	
		3.63		0.64	
	4.78	1.53	25	0.30	
			35	0.48	9.78
			40	0.52	
Pd-D	1.52			0.28	
	3.03	1.53	30	0.41	
	4.54			0.49	
	6.06			0.61	
	3.03	0.90	30	0.24	
		2.30		0.54	
		3.63		0.64	
	3.03	1.53	25	0.39	
			35	0.47	7.19
			40	0.58	

[a] Reaction conditions: solvent = 20 mL of methanol; pH$_2$ pressure = 1 atm.

TABLE VIII
Effect of Pressure on Hydrogenation at 27°C[a]

Catalyst	H_2 pressure (psi)	Cyclooctane yield (%)[b]
Pd-A	20	2.7
	30	6.2
	40	10.1
Pd-B	20	3.1
	30	7.2
	40	10.8
Pd-C	20	7.3
	30	8.1
	40	12.0
Pd-D	20	8.0
	30	9.4
	40	12.8

[a] Reaction conditions: catalyst weight = 100 mg; solvent = 20 mL of methanol; *cis*-cyclooctene = 10 mmol; time = 24 h.
[b] Yield based on *cis*-cyclooctene taken.

TABLE IX
Effect of Pressure on Hydrogenation at 50°C[a]

Catalyst	Hydrogen pressure (psi)	Initial rate of hydrogenation (mL/min)	Cyclooctane yield (%)[b]
Pd-A	200	0.67	47.7
	300	0.97	54.8
	400	1.42	59.2
Pd-B	200	0.68	49.0
	300	1.02	58.1
	400	1.82	60.5
Pd-C	200	1.76	68.5
	300	2.25	73.1
	400	2.43	78.1
Pd-D	200	1.82	70.1
	300	2.32	75.3
	400	2.28	78.4

[a] Reaction conditions: catalyst weight = 100 mg; solvent = 20 mL of methanol; *cis*-cyclooctene = 10 mmol; time = 4 h; stirrer speed = 150 rpm.
[b] Yield based on *cis*-cyclooctene taken.

TABLE X
Recycling Study of Pd-A and Pd-C at 27°C

Catalyst	Cycle No	Cyclooctane yield (%)
Pd-A	1	10.1
	2	9.9
	3	9.8
	4	9.6
	5	9.3
	6	8.0
Pd-C	1	12.0
	2	11.9
	3	11.8
	4	11.4
	5	10.9
	6	8.2

[a] Reaction conditions: catalyst weight = 100 mg; *cis*-cyclooctene = 10 mmole; pH$_2$ pressure = 40 psig; time = 24 h.

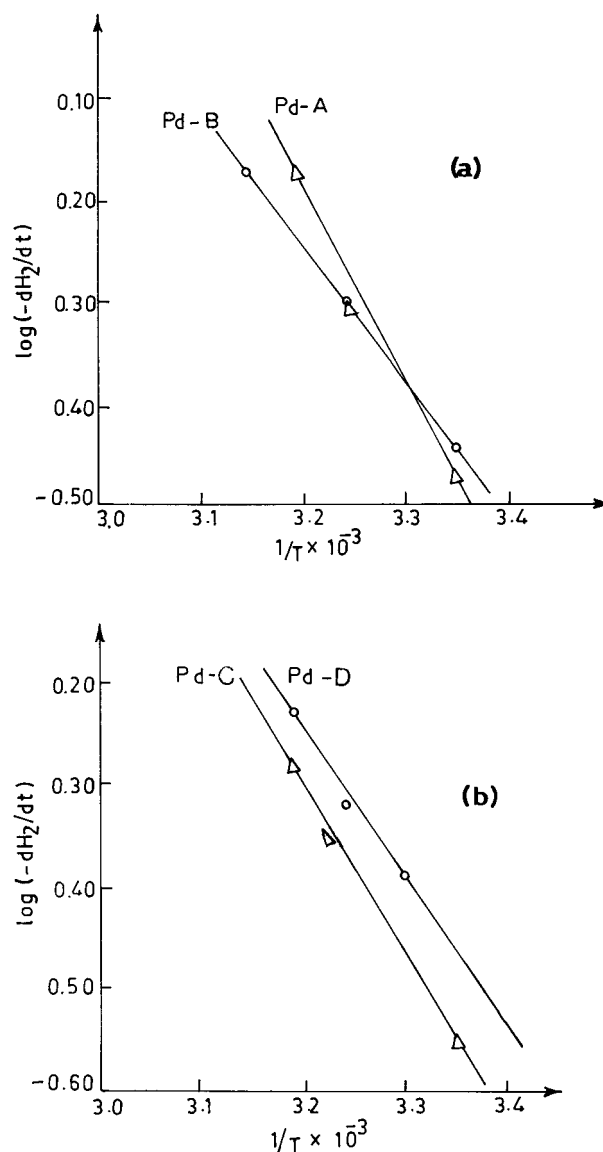**Figure 4** Temperature versus $\log(-dH_2/dt)$ of the Pd catalysts.

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