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PREPARATION, PROPERTIES, AND CATALYTIC APPLICATION OF POLYMER-BOUND Ru(III) COMPLEXES

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ABSTRACT

Styrene–divinylbenzene copolymer with 2 and 5% crosslinking was chloromethylated by HCl and HCHO using $AlCl_3$ as the catalyst. Polymer-bound Ru(III) complex catalysts were synthesized by sequential attachment of 1,2-diaminopropane to the copolymer beads followed by treatment with a metal salt. The catalysts were characterized by using various techniques: FT-IR, SEM, EPR, NMR, ESCA, TGA, and UV-Vis reflectance spectroscopy. Other physicochemical properties were determined: surface area by the BET method, swelling studies with different solvents, and moisture content. The catalytic behavior of the prepared catalysts was tested for hydrogenation of cyclohexene as a model reaction. The influence on catalytic behavior of various parameters was studied: temperature, concentration of catalyst and substrate, quantity of solvent, and the use of various solvents. The recycling efficiency of the catalysts was also studied. A probable reaction mechanism is proposed.

INTRODUCTION

Heterogenizing a homogeneous metal complex by supporting it on a polymer has received wide attention in recent years. Research directed toward catalysis by supported transition metal complexes has become an area of intense interest [1-4]. Many researchers have studied and compared the behavior of transition metal complexes as catalysts in homogeneous and heterogenized states, mainly because of their higher catalytic activity under mild operating conditions [5-8]. The present study was undertaken to synthesize chelated ruthenium metal complexes on a polymeric support and to study their catalytic activity for the hydrogenation of cyclohexene as a model reaction.

EXPERIMENTAL

Materials and Equipments

Styrene, divinylbenzene (DVB), dioxane, methanol, and cyclohexene were purified according to published methods [9]. 1,2-Diaminopropane and 1,2-dichloroethane were distilled before use. Aluminum chloride was purified by sublimation. $RuCl_3 \cdot 3H_2O$ (Lobachemie, Bombay) was used without purification.

UV-Vis reflectance spectra of the solid samples were recorded on a Shimadzu UV-240 Spectrophotometer with reference to nonabsorbing $BaSO_4$ as a standard and liquid sample in methanol. FT-IR and NMR were recorded on a Perkin-Elmer R-32 Instrument. The surface area of the support as well as of the catalysts was measured using a Carlo-Erba Strumentzione 1800. Elemental analyses and TGA were carried out in our laboratory on a Coleman Analyser and a Shimadzu Thermal Analyzer DT-30, respectively. SEM were recorded on a Jeol Scanning Microscope JSM T-300. ESR was scanned on a Breaker ESP-300K, and ESCA was recorded on VG Model ESCA-3 Mark(II) U.K. with $AlK\alpha$ and $MgK\alpha$ as the radiation sources.

Swelling studies of the catalysts were carried out using polar and nonpolar solvents at constant temperature. The detailed procedure has been described earlier [10].

Synthesis of Polymer-Supported Catalysts

Styrene-divinylbenzene copolymer with 5% crosslinking was synthesized by the suspension polymerization technique using benzoyl peroxide as the initiator [10]. After polymerization the beads were washed with distilled water, a water-ethanol mixture (1:1), and ethanol, and finally Soxhlet extracted with an ethanol-benzene (1:1) mixture for 20 hours. In a separate set of experiment, commercially available styrene-divinylbenzene copolymer with 2% crosslinking (XAD-2) was taken as a polymer support. The polymer beads were chloromethylated with HCl, paraformaldehyde, and acetic anhydride using 1,2-dichloroethane as the solvent in the presence of $AlCl_3$ as the catalyst [11]. C, H, and Cl were found to be 76.18, 7.39, and 9.80% in 5% crosslinked polymer and 62.77, 7.47, and 5.70% for XAD-2 using a Coleman Elemental Analyser.

In order to introduce the ligand, a solution of 1,2-diaminopropane in ethanol was kept in contact with chloromethylated polymer beads at 60°C for 8 hours. The percentage of nitrogen was found to be 2.73 and 1.68 for 5% crosslinked and XAD-2, respectively, thereby confirming loading of the ligand.

The functionalized beads were kept in contact with an ethanolic solution of $RuCl_3 \cdot 3H_2O$ for 7 days. The experimental procedure for anchoring the metal ion is reported elsewhere [1]. The metal content was determined by refluxing the metal-containing polymer beads with concentrated HCl (AR) for 24 hours and then estimating the metal concentration in the solution by a spectrophotometric method after complexation with a nitroso-R salt [12]. Catalysts thus prepared were defined by NPML, where N = percent crosslinking, P denotes the copolymer of styrene-divinylbenzene, M is the metal (which is Ru in this case), and L is the ligand (i.e., 1,2-diaminopropane, DAP). The following two catalysts were prepared:

Catalyst A = 5 P Ru(III) DAP
Catalyst E = 2 P Ru(III) DAP

Kinetics of Hydrogenation

The kinetics of hydrogenation of cyclohexene was studied at atmospheric pressure by measuring the hydrogen uptake using a glass manometric apparatus. The detailed procedure and experimental set-up are described elsewhere [10, 13]. The product was analyzed by gas chromatography. The initial rate was calculated from the slope of the plot of H_2 uptake at various time intervals.

RESULTS AND DISCUSSION

Physicochemical properties of the supported catalysts are given in Tables 1a, 1b, and 1c. A decrease in surface area was observed after loading the metal ions on the polymer support. This might be due to blocking of pores of the polymer support after introduction of the ligand and metal ion. The change in morphology is also depicted in SEM (Fig. 1). Similar results were obtained earlier [10, 14–16]. Elemen-

TABLE 1a. Physiochemical Properties of the Supported Catalysts: Physical Properties

	Catalyst[a]	
Physical properties	A	E
Pore volume ($mL \cdot g^{-1}$)	0.209 (0.212)	0.42 (0.42)
Surface area ($m^2 \cdot g^{-1}$), NTP	8.72 (9.78)	298.42 (330.00)
Apparent bulk density ($g \cdot cm^{-3}$)	0.45	0.37
Moisture content (wt%)	1.62	0.40

[a] Values for the polymer support are shown in parentheses.

TABLE 1b. Physicochemical Properties of the Supported Catalysts: Elemental Analyses at Different Stages of Preparation (in wt%)

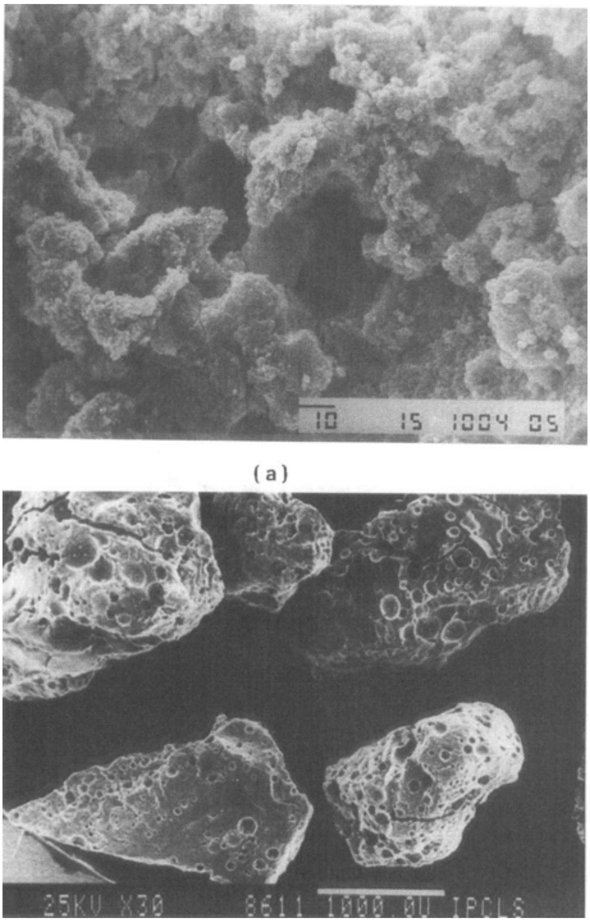
	X[a]			Y[b]			Z[c]			
Catalyst	C	H	Cl	C	H	N	C	H	N	Ru
A	76.18	7.31	9.8	72.20	7.48	2.73	71.62	7.28	2.51	3.75×10^{-2}
E	62.77	7.47	5.7	61.01	7.28	1.68	61.76	7.35	1.44	3.20×10^{-3}

[a] X = after chloromethylation.
[b] Y = after ligand introduction.
[c] Z = after complex formation.

tal analyses at different stages of catalyst preparation indicate the successful functionalization of the polymer (Tables 1a and 1b). Maximum swelling in water might be due to hydrogen bonding of water with amino groups. Methanol was used for the hydrogenation reaction as it was observed to be a better swelling agent. A decrease in swelling was observed as the nature of the solvent was changed from polar to nonpolar. However, an increase in swelling was found with the degree of crosslinking of the polymer support, thereby reflecting the rigidity of the catalyst [8, 10]. Catalyst E exhibited more swellability than Catalyst A. A change in the morphology of the catalysts as well as the support was seen by using a scanning electron microscope (Fig. 1). It was observed that the beads were porous and that the texture changed with a change in the degree of polymer crosslinking. A clear change in morphology was observed on loading the metal complex. The UV-Visible reflectance spectra of both catalysts show d-d transitions of Ru(III) at 230 and 270 nm. In the case of the homogeneous complex [RuDAPCl$_2$]Cl, the peaks appeared at 230 and 270 nm, confirming the presence of Ru(III) in the same oxidation states in both the homogeneous and heterogenized homogeneous systems. The EPR spec-

TABLE 1c. Physicochemical Properties of the Supported Catalysts: Swelling Studies

	Swelling (mol%)	
Solvent	Catalyst A	Catalyst E
Water	0.73	1.21
Methanol	0.68	1.12
Ethanol	0.47	0.61
Dioxane	0.21	0.51
DMF	0.14	0.50
Acetone	0.13	0.49
THF	0.11	0.48
Benzene	0.10	0.32
n-Heptane	0.06	0.11



(a)

(b)

FIG. 1. Scanning electron micrograph of (a) polymer support (styrene-divinylbenzene copolymer with 5% crosslinking) and (b) Catalyst A.

trum of the unbound Ru complex gave $g_{\perp}$, $g_{\parallel}$, and g_{av} values of 1.897, 2.504, and 2.360, respectively, which shows Ru is present in the low spin +3 oxidation state. This has been confirmed by ESCA studies where the polymer-bound catalysts gave peaks due to Ru(3d 3/2), Ru(3p 3/2), N(1s), Cl(2p 3/2), and C(1s) for ruthenium-DAP, indicating the +3 oxidation state of the polymer. The NMR spectrum of the ligand 1,2-DAP showed two peaks at 1.0 and 2.42 due to amino and methylene protons, respectively. The NMR of the unbound complex [RuDAPCl$_2$]Cl shows that the peak due to methylene proton is shifted by 0.2, and the amino proton peak appeared in the same region with multiple splitting. This indicates a different electronic environment of the ligand after complexation. The mode of anchoring the metal ion on the polymer matrix was confirmed by FT-IR. The various IR frequencies are assigned as ν(Ru—Cl) = 250 cm^{-1}, ν(Ru—N) = 320 cm^{-1}, ν(C—N) = 1030 cm^{-1}, ν(N—H) = 3420 and 1630 cm^{-1}, and ν(—CH$_2$Cl) = 1265

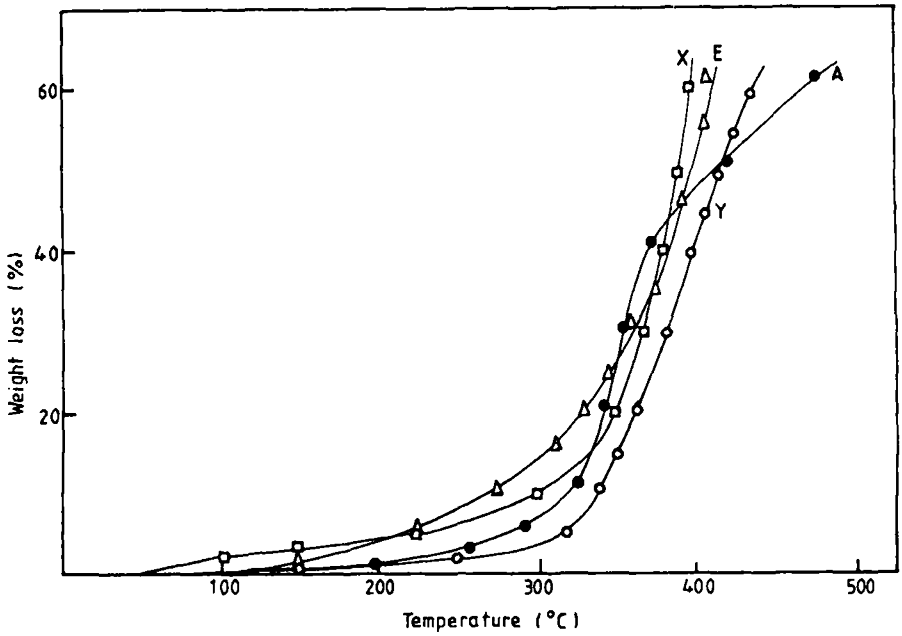
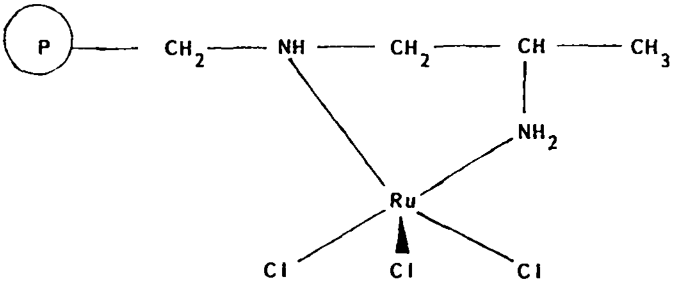


FIG. 2. TG curves of polymer supports and catalysts [X = 2% P(S-DVB) and Y = 5% P(S-DVB)].

cm^{-1} for Catalyst A; and ν(Ru—Cl) = 241 cm^{-1}, ν(Ru—N) = 322 cm^{-1}, ν(C—N) = 1044 cm^{-1}, ν(N—H) = 3440 and 1602 cm^{-1}, and ν(—CH$_2$Cl) = 1271 cm^{-1} for Catalyst E. This confirms the formation of a metal complex on the surface of the polymer.

The thermal stability of the polymer supports was observed to increase on increasing the crosslinking of the polymer, as was seen by TGA studies. No change was observed when a metal complex was loaded on the support (Fig. 2). The initial weight loss might be due to moisture content, and degradation of the polymer starts above 100°C. Based on the spectroscopic evidence, a probable structure of the catalyst is shown in Scheme 1.



SCHEME 1.

Hydrogenation Reaction

The kinetics of hydrogenation of cyclohexene for polymer-supported Catalysts A and E were investigated. The data for the hydrogenation reaction were obtained in a kinetic regime using a stirring speed of 700 rpm in the 30 to 45°C temperature range. The rate of hydrogenation in each run was calculated from the slope of plots of the volume of H_2 absorbed (STP) as a function of time, and a summary of results is given in Tables 2–4. The effect of various parameters on the rate is discussed on the basis of experimental observations.

Effects of Cyclohexene Concentration

The effect of concentration of cyclohexene on the rate of hydrogenation reaction was studied at 35°C under a pressure of 1 atm at constant catalyst concentrations of 3.71×10^{-5} and 3.16×10^{-6} mol·L^{-1} of Ru for Catalysts A and E, respectively (Tables 2–4). The substrate concentration was varied from 4.71×10^{-3} to 18.84×10^{-3} mol·L^{-1} for all catalysts. The order of reaction calculated from the linear plots of log(initial rate) vs log(cyclohexene) was found to be fractional. Linear plots of 1/rate vs 1/[cyclohexene] for both catalysts (Fig. 3) show that the

TABLE 2. Summary of Kinetics of Cyclohexene Hydrogenation by Catalyst A in Methanol at Atmospheric Pressure

[Ru], (mol·L^{-1})10^5	[Cyclohexene], (mol·L^{-1})10^3	Temperature, °C	Methanol, mL	Rate of reaction, mL·min^{-1}
3.71	9.42	35	10	0.016
			20	0.021
			25	0.023
			30	0.028
			40	0.032
3.71	4.71	35	20	0.017
	9.42			0.021
	11.77			0.022
	14.13			0.024
	18.84			0.030
1.85	9.42	35	20	0.017
3.71				0.019
4.63				0.027
5.57				0.029
7.42				0.038
3.71	9.42	30	20	0.017
		35		0.023
		40		0.024
		45		0.040

TABLE 3. Summary of Kinetics of Hydrogenation of Cyclohexene by Catalyst E in Methanol at Atmospheric Pressure

[Ru], $(\mathrm{mol \cdot L^{-1}})10^6$	[Cyclohexene], $(\mathrm{mol \cdot L^{-1}})10^3$	Temperature, °C	Methanol, mL	Rate of reaction, $\mathrm{mL \cdot min^{-1}}$
3.16	9.42	35	10	0.018
			20	0.021
			25	0.023
			30	0.028
			40	0.030
3.16	4.71	35	20	0.020
	9.42			0.025
	11.77			0.029
	14.13			0.034
	18.84			0.043
1.58	9.42	35	20	0.020
3.16				0.024
3.95				0.025
4.75				0.029
6.33				0.032
3.16	9.42	30	20	0.020
		35		0.026
		40		0.032
		45		0.050

TABLE 4. Solvent Dependence for the Hydrogenation of Cyclohexene by Supported Catalysts at Atmospheric Pressure and 35°C in 20 mL Solvent

Catalyst	[Ru], $\mathrm{mol \cdot L^{-1}}$	[Cyclohexene], $(\mathrm{mol \cdot L^{-1}})10^3$	Solvent	Rate of reaction, $\mathrm{mL \cdot min^{-1}}$
A	3.71×10^{-5}	9.42	Methanol	0.021
			Ethanol	0.020
			Dioxane	0.015
			THF	0.012
			Benzene	0.007
E	3.16×10^{-6}	9.42	Methanol	0.021
			Ethanol	0.020
			Dioxane	0.017
			THF	0.012
			Benzene	0.006

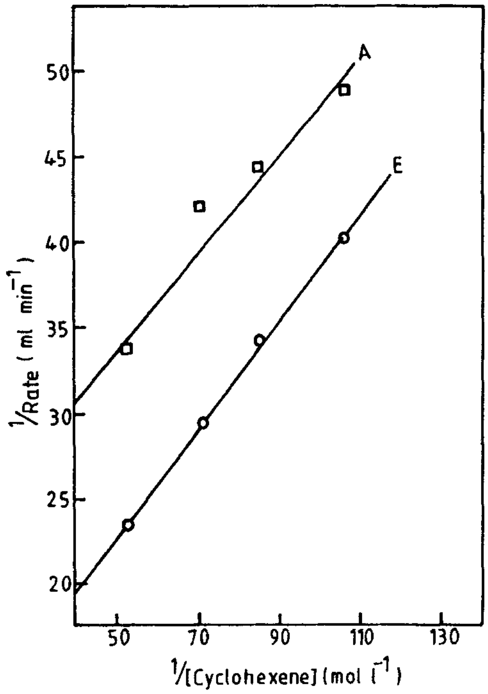


FIG. 3. Plot of 1/rate vs 1/[cyclohexene] for the polymer-bound Catalysts A and E.

rate of hydrogenation of cyclohexene, R, is related to the concentration of cyclohexene, [S], by the relationship

$$\frac{1}{R} = a\frac{1}{[S]} + b$$

where a and b are the slope and intercept of the linear plot.

Effect of Catalysts Concentration

The effect of catalyst concentration on the hydrogenation of cyclohexene was investigated over the range of 1.85×10^{-5} to 7.42×10^{-5} mol·L^{-1} of Ru for Catalyst A and 1.58×10^{-6} to 6.33×10^{-6} mol·L^{-1} of Ru for Catalyst E at a pressure of 1 atm and 35°C with a substrate concentration of 9.42×10^{-3} mol·L^{-1} (Tables 2 and 3). The order of reaction calculated from linear plots of log(initial rate) vs log[catalyst] were found to be fractional with respect to catalyst concentration. This may be due to the nonavailability of catalytic sites and lack of swelling as well as steric hindrance [10].

Effect of Temperature

The study for the rate of hydrogenation was carried out over a temperature range of 30–45°C at catalyst concentrations of 3.71×10^{-5} and 3.16×10^{-6} mol·L^{-1} of Ru for Catalysts A and E, respectively (Tables 2 and 3), and an increase in the rate was observed. The values for the energy of activation calculated from the slope of the plot of log(initial rate) against $1/T$ (Fig. 4) were found to be 48.5 and 51.06 $kJ \cdot mol^{-1}$ for Catalysts A and E, respectively.

Effect of Hydrogen Concentration in Solution

Tables 2 and 3 illustrate the influence of hydrogen concentration in methanol for both catalysts at fixed concentrations of catalysts and substrate at 35°C. It can be seen that the rate increases with increasing volume of methanol and hence of hydrogen concentration.

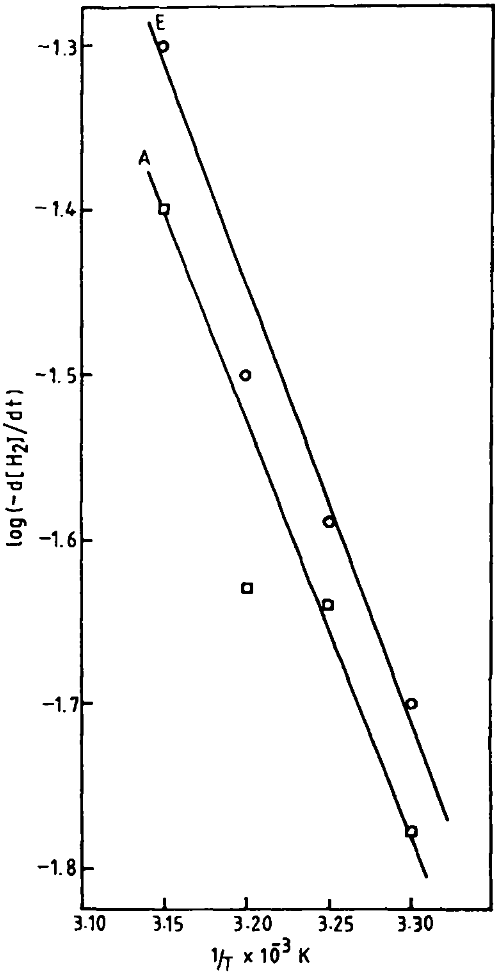


FIG. 4. Arrhenius plots for the catalytic hydrogenation of cyclohexene. Catalyst A: E_a = 48.5 kJ/mol. Catalyst E: E_a = 51.06 kJ/mol.

Effect of Solvent

The effect of five different solvents on the rate of hydrogenation was measured. The rate was found to decrease as the nature of the solvent was changed from polar to nonpolar. The results are given in Table 4. The enhancement in the reaction rate in polar solvents might be due to swelling of the polymer support and hence to the availability of catalytic sites.

Life Cycle of Catalysts

The main objective for supporting metal ions on a polymer support is for reuse of the catalyst. The polymer-bound catalysts can lose their activity by the loss of Ru(III), which is brought about by leaching of the metal complex or reduction to the free metal [8]. In order to study the activity of the catalyst for reuse, the recycling efficiency of the catalysts was tested for both used and fresh catalysts. The experiment was carried out at 35°C for 16 hours by injecting a known amount of substrate (i.e., 10 μL) at 60-minute intervals. The rate of hydrogenation was measured as a function of time for both used and fresh catalysts. It was observed that the maximum rate of reaction was maintained for about 10 hours for Catalyst A, after which the rate decreased slowly (Table 5), whereas in the case of Catalyst E the maximum rate was maintained for 4 hours. The estimation of metal content at the end of the reaction showed a loss of about 50% of the metal from the support in the case of Catalyst A and 63% in the case of Catalyst E. The loss in catalytic activity

TABLE 5. Life Cycle Study of Catalysts A and E at Atmospheric Pressure and 35°C in 20 mL Methanol

Fresh catalysts		Used catalyst	
Time, min	Rate of reaction, $mL\cdot min^{-1}$	Time, min	Rate of reaction, $mL\cdot min^{-1}$
	Catalyst A[a]		
120	0.038	120	0.038
340	0.038	340	0.038
550	0.038	560	0.036
720	0.035	760	0.034
940	0.033	900	0.030
	Catalyst E[b]		
60	0.032	60	0.032
200	0.032	220	0.027
350	0.032	300	0.020
480	0.031		

[a] Amount of catalyst: 0.4 g (7.92×10^{-5} Ru $mol\cdot L^{-1}$). Total time on stream: 15.6 h (15.00 h for used catalyst).

[b] Amount of catalyst: 0.4 g (6.33×10^{-6} Ru $mol\cdot L^{-1}$). Total time on stream: 8.0 h (5.00 h for used catalyst).

may be due to the low mechanical strength of the polymer support or to polymer-bound complexes and polymer-bound noncoordinated ligand molecules leaching out in solution and forming stable complexes in solution which are less effective for catalyzing the reaction.

Rate Equation

The mechanism of olefin hydrogenation over a ruthenium catalyst has been extensively studied. The formation of hydrido species and preferential attachment of the olefin to the ruthenium hydrido complex have been well established by various experimental studies and thermodynamic properties [17]. On the basis of experimental results as well as evidence from the literature, the following mechanism and rate equation are proposed.

$$[\mathrm{RuDAPCl_2}]\mathrm{Cl} + \mathrm{H_2} \overset{K_1}{\rightleftharpoons} [\mathrm{RuDAP(H)Cl}]\mathrm{Cl} + \mathrm{HCl}$$

$$[\mathrm{RuDAP(H)Cl}]\mathrm{Cl} + \mathrm{S} \xrightarrow[\text{slow}]{K'} [\mathrm{RuDAP(HS)Cl}]\mathrm{Cl}$$

$$[\mathrm{RuDAP(HS)Cl}]\mathrm{Cl} + \mathrm{H_2} \xrightarrow[\text{fast}]{} [\mathrm{RuDAP(H)Cl}] + \text{alkane}$$

where K_1 is the equilibrium constant, K' is the rate constant, and S is [cyclohexene].

$$\text{Rate}\,(R) = \frac{K_1K'[\mathrm{C}][\mathrm{H_2}][\mathrm{S}]}{1 + K[\mathrm{S}]}$$

where K is a constant and [C] is the catalyst concentration, i.e., $[\mathrm{RuDAPCl_2}]\mathrm{Cl}$.

CONCLUSION

The ruthenium-1,2-diaminopropane complex was successfully heterogenized by using the PS–DVB copolymer. The attachment and formation of the metal complex on the polymer matrix was confirmed at various stages by carrying out elemental analysis studies, IR, UV-Vis, EPR, and ESCA, and by comparing the results with the unbound complex. A probable structure is proposed but many other possibilities cannot be ruled out. Both the catalysts were found active for hydrogenation of the cyclohexene reaction under mild conditions. A 2% crosslinked supported catalyst is more active than a 5% crosslinked supported catalyst. The main aim of improving the stability of polymer-bound complexes by using chelated ligands was not achieved. This may be due to various types of metal complexes forming on the polymer matrix, of which only a few may be stable during reaction conditions. A more detailed study is needed to confirm this premise.

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