

# Surface characterization and catalytic activity of polymer-anchored Ru(III)–schiffbase complex

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## Abstract

A polymer-anchored Ru(III)–schiffbase complex was synthesized by chloromethylation of styrene-divinylbenzene copolymer with 14% cross-linked (AM-24) followed by sequential attachment of ethylenediamine and salicylaldehyde and finally, treatment with an ethanolic solution of metal salt. It was characterized using various techniques such as FTIR, reflectance UV–Vis spectroscopy, SEM, Electron Spin Resonance (ESR), ESCA and TGA. Various other physico-chemical properties such as bulk density, surface area, moisture content and swellability in different solvents have also been studied. Catalytic activity of the synthesised complex was investigated for hydrogenation of styrene and oxidation of benzylalcohol. Reaction kinetics was studied by varying different parameters. Results were compared with that of unbound metal complex and higher catalytic activity was found in case of supported catalyst. Catalytic behaviour under repeated catalytic cycles was studied. A probable reaction mechanism has been proposed. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Heterogenizing a homogeneous metal complex by supporting it on an insoluble support has attracted a lot of interest as a suitable method for solving many practical problems including recovery of the catalyst from reaction mixture and its reuse [1–3]. Cross-linked polymers are very popular as catalyst supports [4]. We have studied catalytic activity of Ru(III), Rh(I), Rh(III), Pd(II), Co(II), Ni(II), Cu(II) and Mn(II) metal ions anchored onto different polymers [5–10]. Mainly chelating amines were used

as ligands and hydrogenation of olefins was studied as a model reaction to check catalytic activity of these complexes under mild operating conditions. It could be interesting to use a ligand with N and O donor groups. Styrene is an interesting compound to investigate catalytic performance at a laboratory scale because of the presence of two types of unsaturated groups [11]. Oxidation of alcohols is a useful method for preparation of aldehydes and ketones. Benzylalcohol oxidation using zeolites and metal oxides has been reported by many researchers [12–14]. However, not many reports are available in literature on the oxidation of benzylalcohol over a polymer-bound catalyst and also use

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of such catalyst for different reactions. It was therefore planned to heterogenize a Ru(III) complex catalyst on the surface of styrene-divinylbenzene copolymer using schiffbase salicylaldehyde-ethylenediamine as a ligand, and to investigate the catalytic activity of this catalyst for two different reactions: hydrogenation of styrene and oxidation of benzylalcohol.

## 2. Experimental

### 2.1. Materials

Styrene-divinylbenzene copolymer with 14% cross-linked (AM-24) obtained from Ion Exchange (India), Bombay was purified by soxhlet extraction using ethanol–benzene (1:1) mixture and dried at 70°C. THF dioxane, methanol, styrene and benzylalcohol were purified according to reported procedure [15]. Ethylenedia-

mine, 1,2-dichloroethane and salicylaldehyde were distilled before use. Aluminium chloride was purified by sublimation.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Lobachemie, Bombay) was used as received.

### 2.2. Synthesis of the catalyst

The purified AM-24 polymer beads was chloromethylated with HCl, paraformaldehyde using 1,2-dichloroethane as a solvent and anhydrous  $\text{AlCl}_3$  as a catalyst at 80°C for 24 h [16]. The detailed procedure for the synthesis and characterization of polymer-bound Ru(III)–schiffbase complex using chloromethylated P(S-DVB) has been described earlier [17]. Synthesised catalyst was named as: catalyst E = 14 PRu(III)salen.

The unbound complex [Ru(III)salen Cl] was obtained in solution by mixing 1:1 mixture of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and salen in methanol which was used to study kinetics of catalytic reactions.

Table 1  
Physico-chemical properties of the supported catalyst

<i>(a) Physical properties</i>				
Surface area (NTP) ( $\text{m}^2 \text{g}^{-1}$ )	75.69(62.030)			
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.279(00.098)			
Apparent bulk density ( $\text{g cm}^{-3}$ )	0.419(00.390)			
Moisture content (wt.%)	1.608			
Values for the polymer support.				
<i>(b) (i) Elemental analysis at different stages of preparation (wt.%); (ii) Concentration of Ru(III) present on the surface: <math>2.97 \times 10^{-3}</math></i>				
	C	H	Cl	N
14% P(S-DVB) $\text{CH}_2\text{Cl}$	80.84	7.42	4.70	–
14% P(S-DVB)salen	87.35	7.74	–	1.45
Catalyst E	71.48	6.20	–	0.34
<i>(c) Swelling studies using different solvents</i>				
Solvent	Swelling (mol%)			
	Polymer support	Catalyst E		
Water	3.83	4.20		
Methanol	2.30	1.91		
Ethanol	1.78	1.39		
Dioxane	1.32	0.90		
<i>N,N'</i> Dimethyl formamide (DMF)	1.13	1.04		
Acetone	1.02	1.12		
THF	0.91	0.78		
Benzene	0.57	0.66		
<i>n</i> -Hexane	0.48	0.34		

### 2.3. Kinetics of catalytic reactions

The kinetics of hydrogenation of styrene and oxidation of benzylalcohol were studied at atmospheric pressure by measuring hydrogen/oxygen uptake using a glass manometric apparatus. The detailed procedure and experimental set-up are described earlier [10]. The initial rate was calculated from the slope of the plot of  $H_2/O_2$  uptake at various time intervals. Styrene was hydrogenated to ethylbenzene and benzylalcohol was oxidised to benzaldehyde. No other side products were formed as revealed by GC analysis.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

Physico-chemical properties of the supported catalyst are given in Table 1. An increase in the

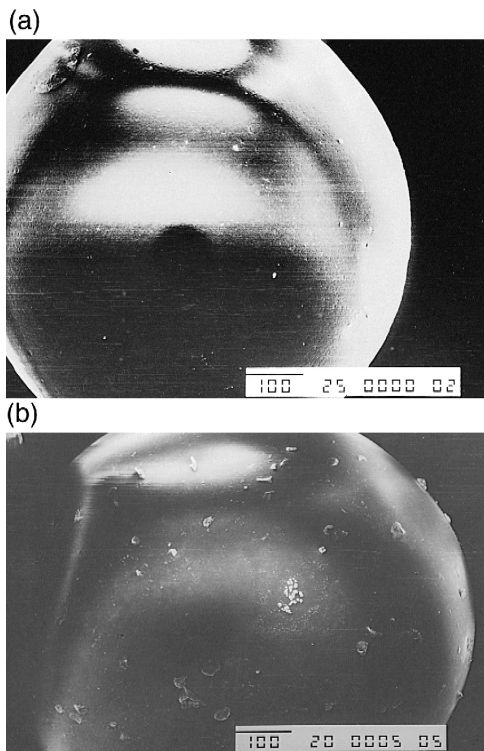


Fig. 1. Scanning electron micrographs of (a) 14% cross-linked P(S-DVB), (b) Catalyst E.

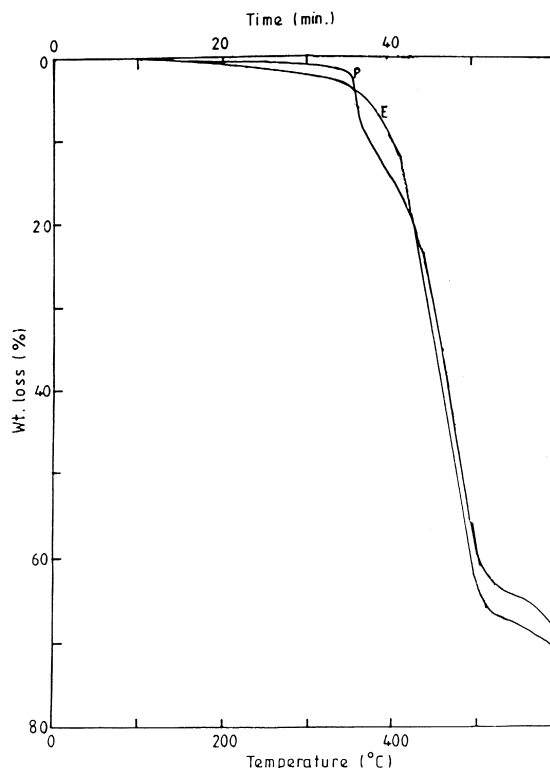
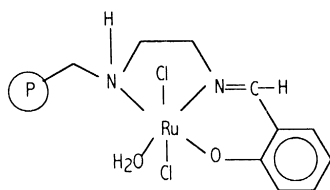


Fig. 2. TGA curves of (P) polymer support (E) polymer-anchored catalyst.

surface area was observed after loading the metal ions, which might be due to functionalization of the polymer with a bulky ligand [18]. Successful functionalization of the polymer was confirmed by elemental analyses at different stages of preparation of the catalyst (Table 1b). A decrease in swelling was observed as the nature of the solvent was changed from polar to non-polar (Table 1c). Maximum swelling was observed in water which might be due to hydrogen bonding of water molecules with amino groups. However, methanol was chosen as a suitable solvent for catalytic reactions because of better swellability with the catalyst and miscibility with the substrate. A clear change in the morphology of the polymer support after introduction of ligand and metal ions was observed by SEM (Fig. 1). The UV–Vis reflectance spectra showed d–d transitions at 400 nm which might be due to Ru(III).  $g$  value was found to



Scheme 1.

be 2.54 from Electron Spin Resonance (ESR) spectra of catalyst E. This is in agreement with a low spin  $d^3$  centre in a square planar environment. ESCA studies of the catalyst gave peaks due to Ru(3p 3/2), Ru(3d 5/2), C(1s), Cl(2p) and N(1s) indicating the presence of Ru in low spin +3 oxidation state. A peak obtained at  $1610\text{ cm}^{-1}$  in IR spectra of polymeric ligand and catalyst E could be assigned due to azomethine group (C=N) of schiffbase. In addition to (C=N), FTIR spectrum of catalyst E also gave peaks at 283, 315 and  $420\text{ cm}^{-1}$  which could be assigned to (Ru–Cl), (Ru–O) and (Ru–N), respectively. This confirms formation of metal complex on the surface of polymer. TG analysis (Fig. 2) showed that thermal stability of the polymer support and the catalyst E is upto  $350^\circ\text{C}$ . The probable structure of the catalyst E was suggested on the basis of spectroscopic studies (Scheme 1).

### 3.2. Catalytic reactions

The kinetics of hydrogenation of styrene and oxidation of benzylalcohol for polymer-anchored catalyst E and homogeneous complex [Ru(III)salen Cl] was investigated. The reaction was

carried out in a kinetic regime at atmospheric pressure in the temperature range of  $25\text{--}45^\circ\text{C}$ . The stirring of the reaction mixture was maintained at an optimized rate (600 rpm) throughout the experiment to minimise diffusion [19]. The influence of various parameters on the rate of reactions was studied.

#### 3.2.1. Hydrogenation of styrene

The effect of substrate concentration on the rate of hydrogenation was determined in the range of  $4.36 \times 10^{-3}$  to  $17.4 \times 10^{-3}\text{ mol l}^{-1}$  at  $35^\circ\text{C}$  and 1 atm pressure at constant catalyst concentration of  $2.97 \times 10^{-6}\text{ mol l}^{-1}$  of Ru(III) (Table 2). It was observed that the rate of hydrogenation increases linearly with respect to substrate concentration. The order of reaction calculated from the linear plot of  $\log$  (initial rate) vs.  $\log$  [styrene] was found to be unity. A linear plot of  $1/\text{rate}$  vs.  $1/[\text{styrene}]$  indicates that the rate of hydrogenation of styrene,  $R$ , is related to the concentration of styrene,  $[S]$ , by the relationship:

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

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

The effect of [catalyst] on the rate of hydrogenation of styrene was studied in the range of  $1.48 \times 10^{-6}$  to  $5.94 \times 10^{-6}\text{ mol l}^{-1}$  of Ru(III) at  $35^\circ\text{C}$  and 1 atm pressure and constant [styrene] of  $8.73 \times 10^{-3}\text{ mol l}^{-1}$  (Table 3). A linear increase in the rate of reaction was found with increase in [catalyst] indicating absence of any

Table 2

Effect of substrate concentration on the hydrogenation of styrene at  $35^\circ\text{C}$ , 1 atm pressure using 20 ml methanol as a solvent; (a) by polymer-bound catalyst, (b) by homogeneous complex [Ru(III)salen Cl]

[Ru(III)] ( $\text{mol l}^{-1}$ )		[Styrene] ( $\text{mol l}^{-1}$ ) $10^3$	Rate of reaction ( $\text{ml min}^{-1}$ )	
$a \times 10^6$	$b \times 10^3$		$a$	$b$
2.97	1.03	4.36	0.07	0.12
		8.73	0.22	0.21
		13.09	0.38	0.32
		17.46	0.54	0.41

Table 3

Effect of [Catalyst] on hydrogenation of styrene at 35°C, 1 atm pressure using 20 ml methanol; (a) by polymer-bound catalyst; (b) by homogeneous complex

[Styrene] (mol l <sup>-1</sup> )10 <sup>3</sup>	[Ru(III)] (mol l <sup>-1</sup> )		Rate of reaction (ml min <sup>-1</sup> )	
	a × 10 <sup>6</sup>	b × 10 <sup>3</sup>	a	b
8.73	1.48	1.03	0.09	0.21
	2.97	2.05	0.22	0.26
	4.45	3.08	0.36	0.31
	5.94	4.10	0.50	0.40

dimerization of metal complex in the range studied. The order of reaction calculated from the plot of log (initial rate) vs. log [catalyst] was found to be unity indicating the availability of all the probable active sites for the catalytic reaction. Thus, better dispersion on the surface could be achieved.

The kinetics of hydrogenation of styrene was studied in the range of 30–45°C at a fixed catalyst concentration of  $2.97 \times 10^{-6}$  mol l<sup>-1</sup> of Ru(III) at 1 atm pressure and [styrene] of  $8.73 \times 10^{-3}$  mol l<sup>-1</sup> (Table 4). An increase in the rate with temperature was found. Energy of activation calculated from Arrhenius plot (Fig. 3) was found to be 104.7 kJ mol<sup>-1</sup> and corresponding entropy of activation was found to be -148.4 eu.

The rate of hydrogenation of styrene was found to decrease as the nature of the solvent was changed from polar to non-polar (Table 5). Higher rate of reaction in polar solvents might be due to better swelling of the polymer support and therefore, availability of catalytic sites.

Kinetics of styrene hydrogenation was also studied using [Ru(III)salen Cl] complex obtained in solution (Tables 2–4). A lower uptake

of H<sub>2</sub> was obtained as compared to heterogenized catalyst even though a 10<sup>3</sup> times higher concentration of metal ion was taken for conveniently measuring the rate of reaction. Energy of activation was found to be 72.8 kJ mol<sup>-1</sup>.

### 3.2.2. Life cycle study of the catalyst

Recycling efficiency of catalyst E was tested at 35°C by injecting a known amount of substrate (i.e. 20 μl) at every 55-min intervals. The rate of reaction was measured as a function of time for both used and fresh catalyst up to 6 h (Table 6). It was found that the maximum rate of reaction was maintained for 3–5 h for fresh catalyst after which it decreased slowly. This might be due to leaching of metal ions from the surface of the polymer.

### 3.2.3. Rate equation

The reaction mechanism for catalytic hydrogenation in homogeneous medium is studied widely. The formation of hydrido species, and preferential attachment of substrate to this intermediate complex has been well established by experimental studies and thermodynamic properties [20]. On the basis of evidence from litera-

Table 4

Effect of temperature on hydrogenation of styrene at 1 atm pressure using 20 ml methanol; (a) for polymer-bound catalyst, [Ru(III)] =  $2.97 \times 10^{-6}$  mol l<sup>-1</sup>, (b) for homogeneous complex, [Ru(III)] =  $1.03 \times 10^{-3}$  mol l<sup>-1</sup> [styrene] =  $8.73 \times 10^{-3}$  mol l<sup>-1</sup>

Temperature (°C)	Rate of reaction (ml min <sup>-1</sup> )		Energy of activation (kJ mol <sup>-1</sup> )		Entropy of activation (eu)	
	a	b	a	b	a	b
30	0.09	0.12				
35	0.22	0.21	104.7	72.8	-148.4	-10.8
40	0.40	0.31				
45	0.55	0.40				

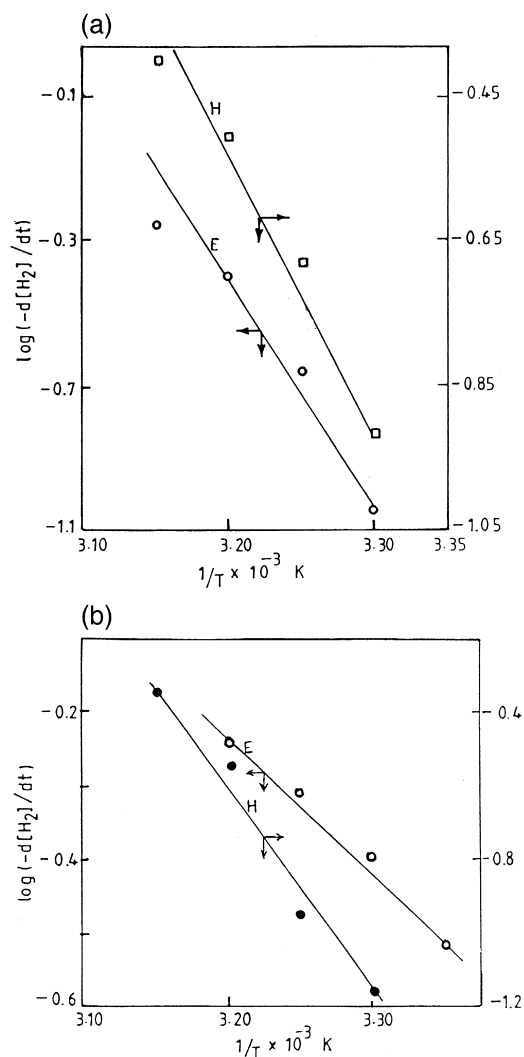


Fig.3. (a) Arrhenius plots for hydrogenation of styrene (E) polymer-anchored catalyst (H) homogeneous complex; (b) Arrhenius plots for oxidation of benzylalcohol (E) polymer-anchored catalyst (H) homogeneous complex.

ture, the following mechanism and rate equation are proposed:

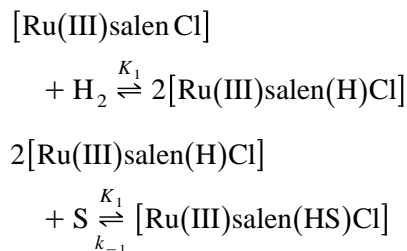
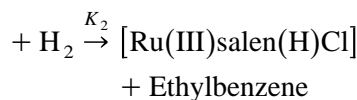


Table 5

Effect of nature of solvent on styrene hydrogenation using polymer-anchored catalyst at 35°C, 1 atm pressure and 20 ml solvent;  $[\text{Ru(III)}] = 2.97 \times 10^{-6} \text{ mol l}^{-1}$   $[\text{styrene}] = 8.73 \times 10^{-3} \text{ mol l}^{-1}$

Solvent	Rate of reaction (ml min <sup>-1</sup> )
Methanol	0.22
Ethanol	0.19
THF	0.10
Benzene	0.07



where  $K$  is equilibrium constant;  $k_1$ ,  $k_{-1}$  and  $k_2$  are the rate constants and  $S$  is styrene:

$$\text{Rate (R)} = K \frac{k_1 k_2 [\text{S}] [\text{H}_2] [\text{C}]}{k_{-1} + k_2 [\text{H}_2]}$$

### 3.2.4. Oxidation of benzylalcohol

The kinetics of oxidation of benzylalcohol for polymer-anchored catalyst E was investigated and the influence of various parameters on the rate of oxidation was studied (Table 7).

The effect of substrate concentration on the rate of oxidation was determined in the range of  $4.83 \times 10^{-3}$  to  $19.32 \times 10^{-3} \text{ mol l}^{-1}$  at 35°C and 1 atm pressure at constant catalyst concentration of  $2.97 \times 10^{-6} \text{ mol l}^{-1}$  of Ru(III) (Table 7). It was observed that the rate of oxidation increases linearly with respect to substrate concentration. The order of reaction calculated from

Table 6

Life cycle study of catalyst E at 35°C and 1 atm pressure using 20 ml methanol;  $[\text{Ru}] = 2.97 \times 10^{-6} \text{ mol l}^{-1}$ ,  $[\text{styrene}] = 8.73 \times 10^{-3} \text{ mol l}^{-1}$  for every injection

Time (min)	Rate of reaction (ml min <sup>-1</sup> )
55	0.22 (0.22)
100	0.22 (0.22)
155	0.22 (0.20)
210	0.21 (0.18)
265	0.18 (0.18)
310	0.15 (0.11)

Values for the used catalysts are indicated in parenthesis.

Table 7

Summary of the kinetics of oxidation of benzylalcohol by catalyst E at 1 atm pressure using 20 ml solvent

[Ru(III)] (mol l <sup>-1</sup> )10 <sup>6</sup>	[Benzylalcohol] (mol l <sup>-1</sup> )10 <sup>3</sup>	Temperature (°C)	Solvent	Rate of reaction (ml min <sup>-1</sup> )
2.97	4.83	35	Methanol	0.31
	9.66			0.49
	14.49			0.65
	19.32			0.79
1.48	9.66	35		0.32
2.97	0.49			
4.45	0.61			
5.94	0.70			
2.97	9.66	25		0.30
		30		0.40
		35		0.49
		40		0.56
2.97	9.66	35	Methanol	0.49
			Ethanol	0.45
			THF	0.30
			Benzene	0.13

the linear plot of log [benzylalcohol] vs. log [styrene] was found to be unity.

The effect of [catalyst] on the rate of oxidation of benzylalcohol was studied in the range of  $1.48 \times 10^{-6}$  to  $5.94 \times 10^{-6}$  mol l<sup>-1</sup> of Ru(III) at 35°C and 1 atm pressure and constant [benzylalcohol] of  $9.66 \times 10^{-3}$  mol l<sup>-1</sup> (Table 7). A linear increase in the rate of reaction was found with increase in [catalyst] indicating absence of any dimerization of metal complex in the range studied. The order of reaction calculated from the plot of log (initial rate) vs. log [catalyst] was also found to be unity.

The kinetics of oxidation of benzylalcohol was studied in the range of 25–40°C at a fixed catalyst concentration of  $2.97 \times 10^{-6}$  mol l<sup>-1</sup> of Ru(III) at 1 atm pressure and [benzylalcohol] of  $9.66 \times 10^{-3}$  mol l<sup>-1</sup> (Table 7). An increase in the rate with temperature was found. Energy of activation calculated from Arrhenius plot (Fig. 3) was found to be 47.9 kJ mol<sup>-1</sup> and corresponding entropy of activation was found to be -28.4 eu.

The rate of oxidation of benzylalcohol was found to decrease as the nature of the solvent was changed from polar to non-polar (Table 7). Higher rate of reaction in polar solvents might

be due to better swelling of the polymer support and therefore, availability of catalytic sites.

Kinetics of oxidation of benzylalcohol using unbound complex [Ru(III)salen Cl] is reported by us earlier and a probable reaction mechanism has already been suggested [17]. The formation of oxo complex and the transfer of oxygen via this route might be responsible for the reaction. The energy of activation was calculated using Arrhenius plots and was found to be 103.4 kJ mol<sup>-1</sup> showing a lower catalytic activity as compared to heterogenized catalyst.

#### 4. Conclusion

The Ru(III)-salen complex was successfully heterogenized using 14% cross-linked P(S-DVB) resin. The attachment and formation of the metal complex on the surface of the polymer was confirmed by elemental analysis, FTIR, UV-Vis, ESR and ESCA. The catalyst was found to be thermally stable up to 350°C. This catalyst was found to be effective for hydrogenation of styrene and oxidation of benzylalcohol. The energy of activation was found to be 104.7 and 47.9 kJ mol<sup>-1</sup>, respectively, for styrene hydro-

genation and benzylalcohol oxidation. Polymer-bound catalyst was found to be more effective towards these catalytic reactions compared to its homogeneous counterpart. However, activity towards oxidation was found to be higher. The catalyst was found to be recyclable up to four cycles in styrene hydrogenation. Formation of intermediate hydrido complex and preferential attachment of substrate to it might be responsible for the reaction.

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