Preparation, Characterization, and Catalytic Activity of Polymer Supported Ethylenediamine and Glycine Cobalt Complexes

D. T. GOKAK, B. V. KAMATH, and R. N. RAM, *Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, India*

Synopsis

Polymer-supported ethylenediamine cobalt chloride and glycine cobalt chloride have been prepared with 2, 5, and 10% divinylbenzene (DVB) styrene copolymer macroporous beads by sequential attachment of the bifunctional ligand followed by treatment of metal salt with the functionalized polymer beads. Physicochemical properties like moisture content, bulk density, swelling, and thermal stability of the supported catalysts have been studied. Probable structures have been proposed based on spectroscopic data obtained from electronic, infrared, far-infrared, and in some cases ESCA. Catalytic activity have been tested for hydrogenation of 1-octene and decomposition of hydrogen peroxide as model reactions.

INTRODUCTION

Catalysis by supported transition metal complexes has gained prominence in recent years.[1-3] Examples of polymer-bound chelated metal complexes are seldom found. Many cobalt and rhodium complexes have been supported on crosslinked polystyrene through phosphine ligands.[4-7] Catalytic activity in these cases was found to decrease on attachment to the polymer, since in most preparations, a percentage of polymer-bound phosphine is left noncoordinated, and this by mass action slows down the reaction rate.[8] Earlier we reported the preparation of various inorganic oxide-supported metal ions and chelated metal complexes[9-13] and their catalytic activity in the decomposition of hydrogen peroxide. In the present paper we report the preparation and characterization of some polymer-anchored chelated metal complexes and their catalytic activity in two model reactions, namely, the decomposition of hydrogen peroxide and hydrogenation of 1-octene.

EXPERIMENTAL

Materials and Equipment

Styrene (S), divinylbenzene (DVB), tetrahydrofuran (THF), dioxane, methanol, 1-ocetene, and *n*-heptane were purified according to published methods.[14] Chloromethyl methyl ether and ethylenediamine were distilled before use. (*Caution* is advised in chloromethylation and in handling of chloromethyl methyl ether because the related compound monochloro ether is

CCC 0021-8995/88/061523-13$04.00

carcinogenic.[15]) Benzoyl peroxide and glycine were recrystallized. Aluminium chloride was purified by sublimation. $CoCl_2 \cdot 6H_2O$ was used without purification.

Ultraviolet spectra of the solid samples were recorded on Shimadzu UV-240, Infrared spectra on Beckmann IR 4220, Far infrared spectra in the region $500-50$ cm^{-1} were recorded at RSIC, Madras. ESCA was recorded on VG model Mark II with AlKα (1486.6 eV) as radiation source and surface area measurements were done on Carlo Erba Strumentzione 1800. Elemental analysis was carried out in our laboratory on Coleman analyzer.

Synthesis of Polymer Support

Macroporous styrene divinylbenzene copolymer with 2, 5, and 10% cross-linking was prepared by suspension polymerization technique by using benzoyl peroxide as initiator.[16] After polymerization the beads were washed with distilled water, water-ethanol mixture (1 : 1), and finally with ethanol. Any adhering material was removed further by soxhlet extraction with ethanol-benzene mixture (1 : 1) for 10 h.

Polymer beads were chloromethylated by a reported procedure[17] using chloromethyl methyl ether. Chloromethylated beads were washed sequentially with 50% aqueous HCl (v/v), dry dioxane, and finally with deionized water until the filtrate was free from chloride ions. Beads were dried at 60–65°C for 24 h under vacuum.

Ligand Attachment to the Chloromethylated Polymers

Chloromethylated polymer beads were kept in contact with tetrahydrofuran (THF) for 30 min in a three-necked 500-mL round-bottom flask fitted with a condenser, mechanical stirrer, and addition funnel. The amount of polymer, THF, and ligand taken in the reaction are respectively:

15 g 70 mL and 5.0 mL; for 10% PSDVB
50 g 170 mL and 16.1 mL; for 5% PSDVB
50 g 200 mL and 15.0 mL; for 2% PSDVB

Ethylenediamine (en) was added dropwise into the reaction vessel over a period of 15 min by using the addition funnel. The reaction was allowed to continue for 48 h with constant stirring at room temperature. The beads were separated by filtration, washed successively with deionized water, methanol, and dry dioxane, and dried at 60°C under vacuum.

A similar procedure was adopted to anchor glycine (gly) ligand on to the polymer. In this case the amount of polymer, THF, distilled water, acetone, and glycine taken in the reaction are, respectively;

20 g 50 mL 50 mL 10 mL 1.60 g for 10% PSDVB
50 g 175 mL 90 mL 10 mL 9.09 g for 5% PSDVB
30 g 200 mL 40 mL 10 mL 10.14 g for 2% PSDVB

The amount of en and gly attached to the polymer was calculated from the elemental analysis (Table I). These results were confirmed by gravimetric

TABLE I
Elemental Analysis and Metal Loading in Different Stages of Reaction

Polymer cross link	A			B			C			
	C Wt%	H Wt%	Cl Wt%	C Wt%	H Wt%	N Wt%	C Wt%	H Wt%	N Wt%	Co Wt%
10%	84.59	7.48	5.55	a 83.92 b 85.21	a 7.30 b 7.02	a 2.73 b < 1.00	a 83.81 b 84.18	a 7.43 b 7.06	a 2.00 b < 1.00	0.288 0.084
5%	78.75	6.39	14.71	a 79.91 b 77.13	a 7.38 b 6.30	a 7.82 b 3.78	a 78.53 b 76.63	a 6.95 b 5.96	a 6.85 b 2.54	0.152 0.044
2%	71.66	5.55	17.71	a 68.60 b 71.25	a 5.88 b 5.42	a 7.80 b 2.26	a 64.66 b 72.38	a 6.05 b 5.50	a 5.57 b 1.26	0.157 0.045

A = after chloromethylation: B = after ligand insertion; C = after complex formation; a = for en liganded; b = for gly liganded.

estimation of chloride[18] present as unreacted chloromethyl group on the polymer support. Amount of en and gly anchored are, respectively, 0.998 and 0.528 mmol g^{-1} for 10% PSDVB, 2.881, and 2.721 mmol g^{-1} for 5% PSDVB, 2.797, and 1.610 mmol g^{-1} for 2% PSDVB.

Complex Formation with the Polymer Anchored Ligand

The functionalized polymer was kept in contact with THF for 30 min in a round-bottom reaction vessel. A solution of $CoCl_2 \cdot 6H_2O$ in THF, taken in an addition funnel fitted to the reaction vessel, was slowly added to the reaction vessel over a period of 30 min. The reaction mixture was stirred mechanically at room temperature for 7 days during which color of the supernatant solution changed from dark blue to light blue and the polymer beads turned dark green in the case on en- and light green in the case of gly-functionalized polymers, which indicated the formation of metal complex on the polymer matrix. Amount of functionalized polymer, THF, and cobalt chloride taken are given below:

Polymer	Amount of functionalized polymer (g)	THF (mL)	$CoCl_2 \cdot 6H_2O$ (g)
P10 en	15	150	1.77
P5 en	43	275	16.65
P2 en	50	350	16.65
P10 gly	15	150	1.25
P5 gly	40	275	16.20
P2 gly	50	350	16.65

The beads were filtered and washed thoroughly with dioxane, methanol, and dry ether. The anchored catalysts so obtained were dried in vacuum and stored.

Cobalt content in each case was determined by refluxing a known amount of polymer-anchored complexes with concentrated hydrochloric acid (AR) for 24 h and then estimating the metal concentration by colorimetry.[19]

Nomenclature

The catalysts were named by the general formula

PNML

where P = copolymer of styrene divinylbenzene (PSDVB)
　　　　N = Percent cross link
　　　　M = Metal atom
　　　　L = Type of ligand

Decomposition of H_2O_2

A known weight of the catalyst was kept in contact with 10 mL ($\sim$ 5 % v/v) of H_2O_2 at 30 $\pm$ 0.1°C and the volume of oxygen evolved was measured by gasometric technique.[10] Experiments were also carried out at different temperatures, different amounts of catalyst, pH, and different concentrations of H_2O_2. Details of the procedure are described elsewhere.[9-12]

Hydrogenation Procedure

Hydrogenation was carried out at atmospheric pressure in a magnetically stirred three-phase semibath glass reactor by using THF (saturated with H_2 at the reaction temperature) as the solvent. After the completion of the reaction the products were analyzed by gas chromatography. The experimental set-up and detailed procedure have been described elsewhere.[20]

High pressure hydrogenation reactions were carried out in the hydrogenation apparatus (Chas W. Cook and Sons Ltd., Birmingham, England) with a stainless steel reaction vessel (125 mL).

Swelling Studies

Measurement of swelling is done by equilibration of the polymer-bound catalyst with the liquid under study.[21] Dried catalyst, 0.5 g, was kept in contact with 25 mL of the liquid for 30 min to attain equilibrium. After equilibration, the catalyst was separated from the bulk liquid. The adhering liquid was removed by centrifugation (15 min, 1000 rpm).. The difference in weights after centrifugation and after complete drying gives the amount of liquid retained.

RESULTS AND DISCUSSION

Surface area and pore volume of the polymer supports measured by BET method are as follows:

Polymer support	Surface area $(m^2 g^{-1})$	Pore volume $(mL\ g^{-1})$
10% PS -DVB	19.1982	0.425
5% PS -DVB	10.354	0.212
2% PS -DVB	3.862	0.085

However, the surface area of supports decreases ($\simeq$ 1 $m^2\ g^{-1}$) after functionalization and complex formation. Attachment of ligands and complex formation of the polymer are evident from elemental analysis, spectral studies, and metal estimation. The loading of the metal ion is less in the case of gly-liganded polymer than in the case of en-liganded polymer. It is observed that complex formation is more favorable in the case of polymers with a higher degree of crosslinking than those with a lower degree of crosslinking.

TABLE II

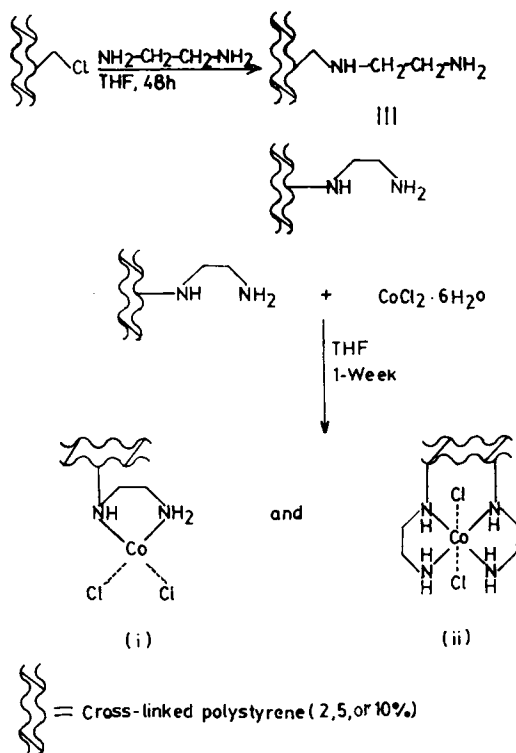| Catalyst	Moisture content (in wt%)	Bulk density g cm^{-3}
P2Coen	1.74	0.584
P5Coen	1.38	0.539
P10Coen	0.95	0.425
P2Cogly	0.70	0.473
P5Cogly	0.52	0.435
P10Cogly	0.46	0.414

This may be due to better conformational arrangement of the macromolecular ligand chain. En-liganded catalysts are found to be hygroscopic and this nature increases with decrease in crosslinking of polymer, so also the bulk density. Gly-liganded catalysts are less hygroscopic (Table II).

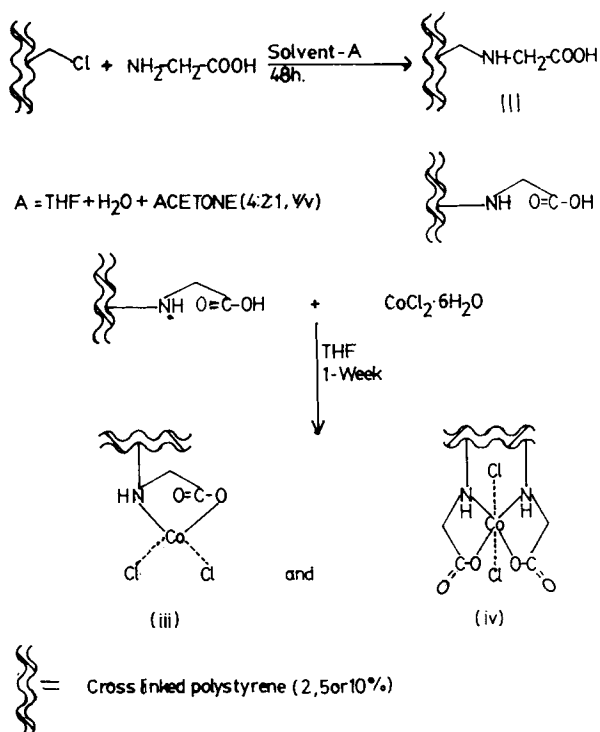## Spectral Characterization of the Catalysts

Infrared spectra of the polymer-anchored complexes are diffuse due to the strong absorption of polymer matrix. In the far-IR region also, absorption bands due to Co—O, Co—N, Co—Cl, are less intense because of low concentration of the metal. However, attempts have been made to assign the bands comparing the spectrum of unbound and polymer-bound complexes[22, 23] as given below:

Complex	Co—N	Co—Cl	Co—O	N—H
Polymer bound Co-en	450 cm^{-1}	320 cm^{-1}	–	3400 cm^{-1}
Unbound Co-en	440 cm^{-1}	270 cm^{-1}	–	3430 cm^{-1}
Polymer bound Co-gly	430 cm^{-1}	320 cm^{-1}	350 cm^{-1} 330 cm^{-1}	3200 cm^{-1}
Unbound Co-gly	440 cm^{-1} 390 cm^{-1}	270 cm^{-1}	370 cm^{-1}	3240 cm^{-1}

The spectra of the polymer-anchored complexes compare well with those of the unbound complexes. Slight shifts in the bands may be due to the change in stereochemistry of the complexes upon anchoring. The absorption due to carbonyl frequency in the case of polymer-bound gly complexes is masked by strong polymer matrix absorption. ESCA and electronic spectra show the presence of nitrogen, oxygen, and cobalt (II) (spectra not given). From the above spectral evidences and physicochemical properties, Scheme 1 and Scheme 2 are proposed to arrive at the possible structure of the catalysts.

$$\text{[polymer]}-CH_2-Cl \xrightarrow[\text{THF, 48h}]{NH_2-CH_2-CH_2-NH_2} \text{[polymer]}-CH_2-NH-CH_2CH_2-NH_2$$

III

[polymer]$-NH$ NH_2

[polymer]$-NH$ NH_2 + $CoCl_2 \cdot 6H_2O$

$\downarrow$ THF
1-Week

(i) and (ii)

[symbol] = Cross-linked polystyrene (2,5,or 10%)

Scheme 1.

[polymer]$-CH_2-Cl$ + $NH_2CH_2COOH \xrightarrow[\text{48h.}]{\text{Solvent-A}}$ [polymer]$-CH_2-NH-CH_2COOH$

III

A = THF + H_2O + ACETONE (4:2:1, V/v)

[polymer]$-NH$ $O=C-OH$

[polymer]$-NH$ $O=C-OH$ + $CoCl_2 \cdot 6H_2O$

$\downarrow$ THF
1-Week

(iii) and (iv)

[symbol] = Cross linked polystyrene (2,5or10%)

Scheme 2.

Swelling Studies

To achieve the higher activity and possibly selectivity in the case of polymer-bound catalytic reactions, it is necessary that the reactant molecules have accessibility to all catalytic sites both on the surface and in the interior of the beads. This requires the use of a solvent in which the polymer has maximum swelling so that the matrix expands sufficiently to allow the reactant molecule to diffuse within the solvent channel and encounter the catalytic centres.

Extent of swelling depends on the solvent-polymer interaction which is determined not only by the nature of the solvent and polymer matrix but also by the active groups introduced into the polymer matrix.

Swelling studies have been carried out for 9 solvents (Figs. 1 and 2). For en-liganded catalysts swelling is maximum in water, which agrees with the hygroscopic nature of this catalyst, and it is minimum in n-hexane. In the case of gly-liganded catalysts swelling is maximum in THF and minimum in n-hexane. Hence THF was chosen as a solvent for catalytic studies.
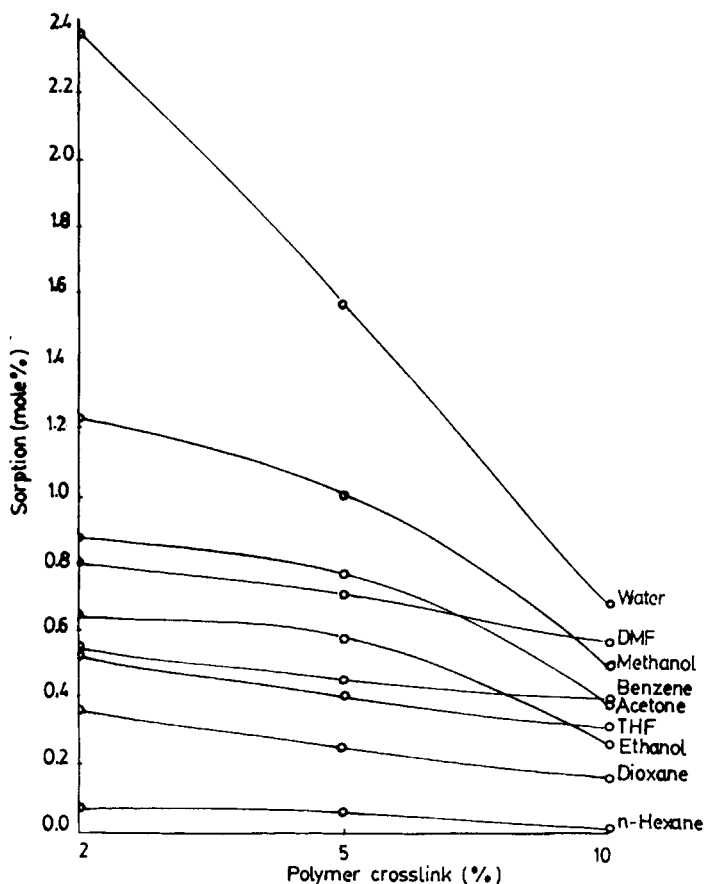

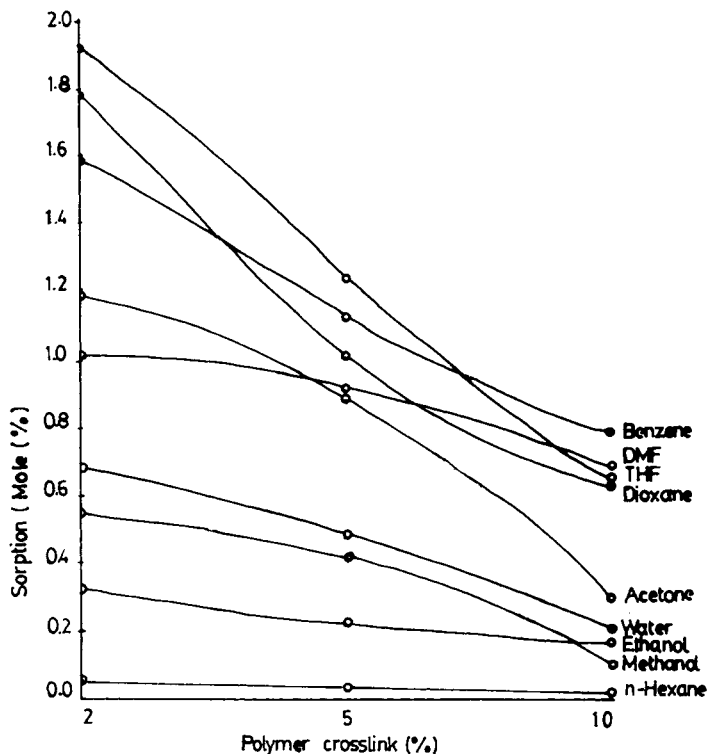Fig. 1.   Swelling studies of polymer-bound cobalt ethylenediamine catalysts.

Fig. 2. Swelling studies of polymer-bound cobalt glycine catalysts.

Decomposition of Hydrogen Peroxide

The supported metal complexes exhibit catalaselike activity.[13, 24] The anchored catalysts have been tested for hydrogen peroxide decomposition (a catalase model) reaction.

PNCoen catalysts are found to be 10 times more active than PNCogly catalysts. The linear plot of $\log(a - x)$ vs. time t (where, a is the volume of oxygen evolved after complete decomposition of H_2O_2 and x that at any time t) in each case indicates that the reaction follows a first-order kinetics with respect to hydrogen peroxide.[9] The values of rate constants calculated from the above plots and the energy of activation calculated by Arrhenius plots are given in Table III. It is clear from the rate constants and activation energy that, although the amount of metal complex anchored was low, the catalytic activities are quite high. The enhanced activity may be attributed to better geometry and attainment of condition of infinite dilution upon anchoring.[25] These catalysts (except P2Coen) when reused for the decomposition studies retain most of their activity, indicating the stability of anchoring of metal chelates. Considerable decrease in the activity of P2Coen catalyst after first cycle might be due to leaching of the metal. This infers that polymer support is also contributing toward the stability of complex. Effects of amount of catalyst, concentration of H_2O_2, and pH have been studied for P2Coen and P5Coen catalysts. An increase in the amount of catalyst and pH increases the

TABLE III
Effect of Temperature on H_2O_2 Decomposition

Catalyst	Amount of metal present (g)	Specific reaction rate (k min^{-1})			Energy of activation (Kcal mol^{-1})
		35°C	45°C	55°C	
P2Coen	5.12×10^{-3}	1.98×10^{-3}	4.86×10^{-3}	1.44×10^{-2}	20.45
P5Coen	6.30×10^{-4}	7.67×10^{-3}	12.90×10^{-3}	2.10×10^{-2}	10.13
P10Coen	1.02×10^{-3}	—	1.63×10^{-3}	3.52×10^{-3}	16.06
P2Cogly	1.91×10^{-3}	6.39×10^{-4}	9.59×10^{-4}	19.19×10^{-4}	10.52
P5Cogly	8.01×10^{-5}	5.75×10^{-4}	8.64×10^{-4}	2.98×10^{-3}	22.10
P10Cogly	4.20×10^{-5}	—	5.00×10^{-4}	1.21×10^{-3}	18.44

TABLE IV
Effect of Concentration of H_2O_2 Temperature: 35°C; Volume of H_2O_2: 10 mL

Catalyst	Amount of metal present (g)	Specific reaction rate (k min^{-1}) for		
		5 Vol.	7 Vol.	10 Vol.
P2Coen	5.12×10^{-3}	1.97×10^{-3}	1.84×10^{-3}	4.60×10^{-3}
P5Coen	6.30×10^{-3}	0.90×10^{-2}	0.84×10^{-2}	1.05×10^{-2}
P2Cogly	1.91×10^{-3}	1.41×10^{-3}	1.77×10^{-3}	1.53×10^{-3}
P5Cogly	8.01×10^{-5}	1.22×10^{-3}	0.60×10^{-3}	1.04×10^{-3}

TABLE V
Effect of Weight of Catalyst Temperature: 35°C; Volume of H_2O_2: 10 mL

Catalyst	Metal content in wt%	Specific reaction rate (k min^{-1}) amount of catalyst used			
		0.2 g	0.5 g	0.7 g	1.0 g
P2Coen	1.020	1.17×10^{-3}	1.79×10^{-3}	3.84×10^{-3}	5.75×10^{-3}
P5Coen	0.315	7.67×10^{-3}	1.90×10^{-2}	2.80×10^{-2}	4.49×10^{-2}
P2Cogly	0.382	0.62×10^{-3}	0.88×10^{-3}	1.06×10^{-3}	1.27×10^{-3}
P5Cogly	0.016	0.52×10^{-3}	0.57×10^{-3}		1.57×10^{-3}

TABLE VI
Effect of pH Temperature: 30°C; Volume of H_2O_2: 10 mL

P2Coen		P5Coen	
pH	Specific reaction rate k min^{-1}	pH	Specific reaction rate k min^{-1}
4.20	1.79×10^{-3}	5.29	2.87×10^{-3}
6.26	1.84×10^{-3}	6.35	4.60×10^{-3}
7.03	3.16×10^{-3}	7.27	7.80×10^{-2}
8.03	10.57×10^{-3}	8.39	7.92×10^{-2}

rate of reaction (Tables V and VI) whereas the rate constant is found to be independent of concentration of H_2O_2 (Table IV).

Hydrogenation Reaction

All the catalysts were tested for 1-octene to *n*-octane model hydrogenation reaction with THF as solvent at atmospheric pressure and also at 2, 3, 4, and 5 atms in each case at 25, 45, and 55°C.

In most cases, the conversion was below 5%. However, P2Cogly catalyst in presence of $NaBH_4$ at 45°C and 3 atm resulted in 10% conversion, whereas P5Coen catalyst in presence of $NaBH_4$ at 55°C and 3 atm pressure resulted in 15% conversion.

It is known that Group VIII transition metal complexes, such as those of Rh and Co, are good catalysts for hydroformylation and hydrogenation of olefins. Gubitosa et al.[26] found that polymer-attached $CpCo(CO)_2$ was an effective hydrogenation and hydroformylation catalyst. Chang et al.[27] have reported that polymer-attached $CpCo(CO)_2$ catalyst was inactive in the case of hydrogenation, isomerization, and hydroformylation reactions. We have also now observed that polymer-attached cobalt catalysts alone when used for
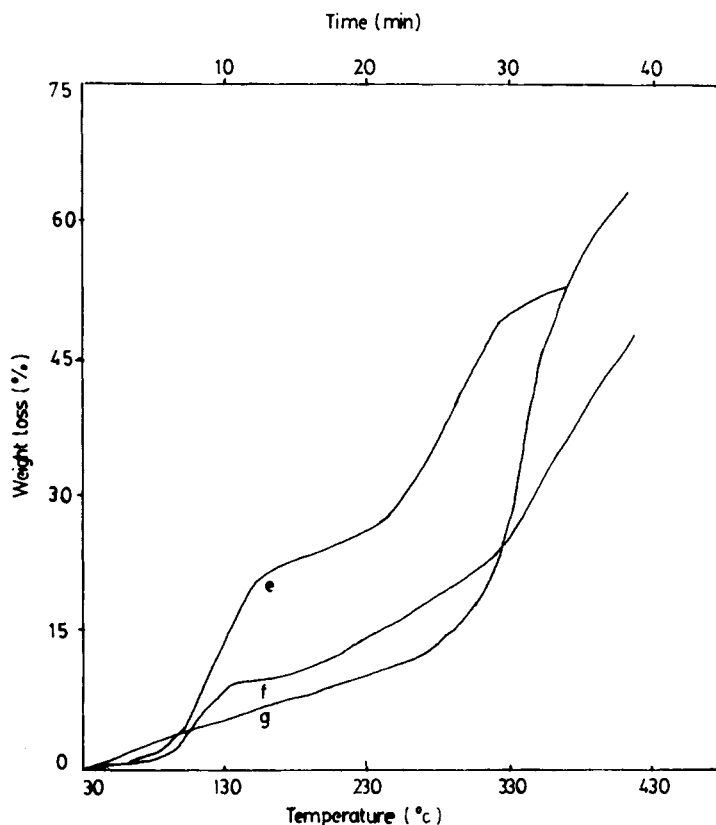

Fig. 3. Thermogravimetric studies of polymer-bound cobalt ethylenediamine catalysts: (1) P10Coen catalyst; (f) P2Coen catalyst; (g) P5Coen catalyst.
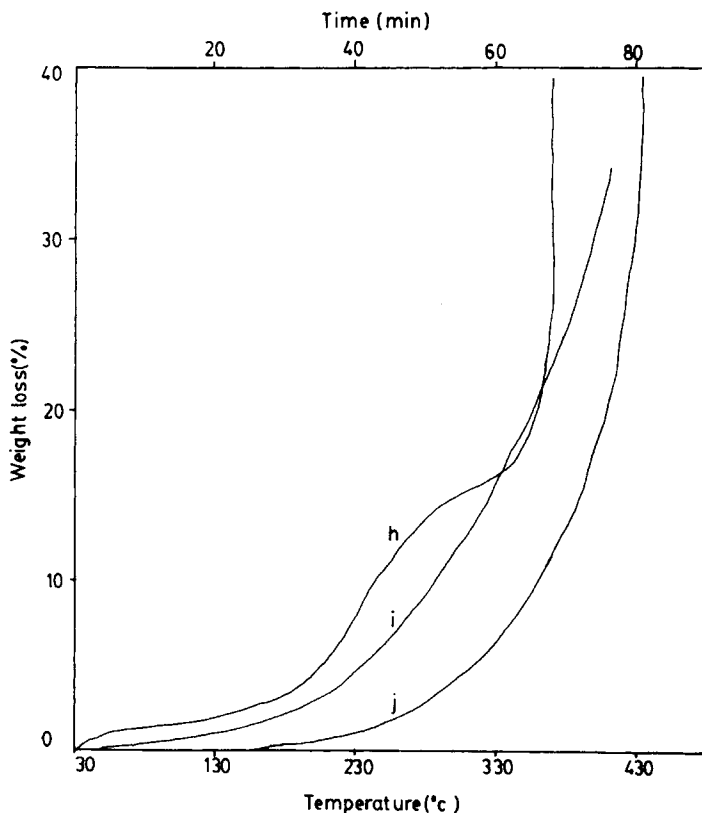
Fig. 4. Thermogravimetric study of polymer-bound cobalt glycine catalysts (h) P5Cogly catalyst; (i) P2Cogly catalyst; (j) P10Cogly catalyst.

the model hydrogenation reaction were inactive whereas, when used in the presence of very small amounts of $NaBH_4$ the activity is improved. Thus we can conclude that formation of cobalt hydride is not easily feasible, but $NaBH_4$ acts as a hydride transferring agent. Further work is in progress in our laboratory.

Thermogravimetric studies of the catalysts (Figs. 3 and 4) show that PNCogly catalysts are more stable than PNCoen catalysts. In both cases the initial weight loss up to 5% may be due to the elimination of moisture, P5Coen and P10Cogly are found to be thermally more stable catalysts.

References

1. Y. Chauvin, D. Commercuc, and F. Dawns, *Progr. Polym. Sci.*, 5, 95–226 (1978).

2. Yu. I. Yermakov, B. N. Kuznetsov, and V. A. Zakharov., *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981.

3. F. R. Hartley, *Supported Metal Complexes*, D. Reidel Publishing Company, Amsterdam, 1985.

4. R. H. Grubbs, *Chemtech*, 512 (1977); C. H. Brubaker, Jr., *Encyl. Polym. Sci. Tech.*, **1**, (Suppl) 116 (1976) and ref. therein.

5. T. Masuda and J. K. Stille, *J. Am. Chem. Soc.*, **100**, 268 (1978) and ref. therein.

6. J. Reed, P. Eisenberger., B. K. Teo, and B. M. Kinacaid, *J. Am. Chem. Soc.*, **100**, 2375 (1978) and ref. therein.

7. F. Pinna, C. Canadilera, G. Strukul, M. Banivente, and M. Graziani, *J. Organometal. Chem.*, **159**, 91 (1978) and ref. therein.

8. J. A. Osborn, F. H. Jardine, and G. Wilkinson., *J. Chem. Soc.*, **A**, 1054 (1968).

9. R. N. Ram, *Ind. J. Tech.*, **23**, 237–240 (1985).

10. R. N. Ram, *Kinetika i Kataliz*, **25**, 1105 (1984).

11. Bhavana Dave, D. T. Gokak, B. V. Kamath, and R. N. Ram, Proceedings of *Second Indo-Sov. Seminar on Catalysis and Catalytic Reaction Engineering*, held at RRL, Hyderabad (India) 268 (1986).

12. D. T. Gokak, B. V. Kamath, and R. N. Ram, *Ind. J. Chem.* **25A**, 1143 (1986).

13. Jatin Shah, D. T. Gokak, B. V. Kamath, and R. N. Ram, *Proc. 8th Natl. Symp. on Catal.* S. K. Nath, Ed., PDIL, Sindri (India) 1987.

14. *Vogel's Text Book of Practical Organic Chemistry*, Longman, ELBS, London, 4th ed., 1978.

15. *The Federal Register* **39** (20), Part III, Occupational Safety and Health Administration "Carcinogens."

16. J. A. Mikes, *Ion Exchange in the Process Industry Conference*. (London, 1969). P. 16 Soc. Chem. Ind. London (1970).

17. R. Kunin, *Ion exchange resins*. John Wiley and Sons, Inc., New York, 1963.

18. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longman, 3rd ed. ELBS, London, 1969.

19. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II, D. V. Nostrand, Inc., Princeton, NJ, 1959.

20. D. T. Gokak, B. V. Kamath, and R. N. Ram, Synthesis and catalytic activity of polymer bound Rh(I) complexes (communicated) 1987.

21. H. P. Gregor, K. M. Held, and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).

22. R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds (3800–45 cm⁻¹)*; Academic Press, New York, 1971.

23. K. Nakamoto, *Spectra of Inorganic and Coordination Compounds*, 3rd ed. John Wiley and Sons, Inc., New York, 1978.

24. H. Sigel, B. E. Wyeas, Fischer, and B. Prija, *Inorg. Chem.*, **18**, 854 (1979).

25. J. C. Bailar, *Cat. Rev. Sci. Eng.*, **10**(1), 17 (1974).

26. G. Gubitosa, M. Boldt, and H. N. Brintzinger, *J. Am. Chem. Soc.*, **99**, 5174 (1977).

27. B. H. Chang, R. H. Grubbs, and C. H. Brubaker, Jr. *J. Organometal. Chem.*, **172**, 81–89 (1979).