

SYNTHESIS AND CATALYTIC PROPERTY OF POLYMER-SUPPORTED Fe-Co HETEROTETRAMETALLIC CLUSTERS

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ABSTRACT

Four polymer-supported Fe-Co tetrametallic clusters have been prepared by ion exchange and ligand exchange. Their structures were characterized by IR, UV/visible diffuse reflectance spectra and elemental analysis, and by analogy with the reference cluster $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_2$. The four heterogenous clusters were efficient catalysts in the hydroformylation of 1-hexene, turnover numbers amounted to 823—924 with the yield of 83.2—92.4% heptyl aldehydes and ratios of normal aldehyde to iso-aldehyde of 1.2—1.6, they are facilitated forming the normal aldehyde in comparison with the homogeneous analogue. For the polymer-supported clusters prepared by ion exchange, the polymer-cation parts had no obvious effect on the activity of the cluster anion. The polymer-phosphine substituted cluster prepared by ligand exchange was more stable than the clusters prepared by ion exchange.

INTRODUCTION

Metal cluster chemistry has entered a period of exponential in the preceding decade, and much of driving force is the prospect of metal clusters as catalysts^[1]. Heteronuclear metal cluster has different reactive sites at different metal centers^[2], and different reaction may be realized at different metals in a cluster^[3]. We have studied the catalytic property of some tri- and tetra-cobalt clusters^[4, 5] and some homogenous heteronuclear clusters^[6, 7]. It was found that Fe-Co tetranuclear clusters have higher catalytic activity because of synergistic effect between Co and Fe in catalytic reaction. In order to study the catalytic behavior of heterogenous Fe-Co clusters, Fe-Co heterotetrametallic cluster was anchored to polymer-ammonium and polymer-phosphonium cation by ion exchange, and anchored to polymer-phosphine by ligand exchange. The polymer-supported clusters were characterized by IR, UV/visible reflectance spectra and elemental analysis. Their catalytic property was investigated in the hydroformylation of 1-hexene.

EXPERIMENTAL

All operations were carried out under nitrogen or argon using conventional inert atmosphere and vacuum techniques. Solvents and olefins were purified and dried by standard method. Published methods were used to prepare $\text{Co}_2(\text{CO})_8$ and $\text{Fe}(\text{CO})_5$ ^[8]; PS/DVB (polystyrene-co-divinyl benzene), PS/DVB- CH_2Cl (chloromethylated PS/DVB, Cl 17.5%, surface area $70 \text{ m}^2\text{g}^{-1}$, and phosphinated PS/DVB (P 7.4%, surface area $63 \text{ m}^2\text{g}^{-1}$)^[9]; and $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_2$ ^[7].

IR spectra were taken on a Perkin-Elmer 983 spectrophotometer, UV/visible diffuse reflectance spectra were measured with a Hitachi 110 spectrophotometer,

using BaSO_4 as standard. Other experimental apparatus and hydroformylation procedure were similar to that used in previous studies⁽⁴⁾.

Preparation of some polymer supports: PS/DVB-CH₂LRR',Cl

General procedure for the preparation of polymer-ammonium salts: 0.01 mol PS/DVB-CH₂Cl and 0.01 mol NRR₂' in benzene (40 ml) were refluxed for 1–4 h and then cooled to room temperature. After filtration, the polymer beads were washed with benzene and ethyl alcohol alternatively and dried afterwards at 40 °C under reduced pressure for 24 h. They are named as Sy, y=1, 2,

S₁: L=N, R=R'=CH₃, X=Cl; Found: N 5.75, Cl 14.57

S₂: L=N, R=CH₃, R'=Ph, X=Cl; Found: N 4.59, Cl 11.64

The polymer-phosphonium salt PS/DVB-CH₂PPh₂CH₃I was prepared as follows: PS/DVB-CH₂PPh₂ (0.01 mol) and CH₃I (0.01 mol) in benzene (40 ml) were refluxed for 10 h and then cooled to room temperature. After filtration, the polymer beads were washed and dried. It is denoted as S₃

S₃: L=P, R=CH₃, R'=Ph, X=I; Found: P 5.76, I 19.99

Preparation of polymer-supported Fe-Co heterotetrametallic clusters

General procedure for the preparation of polymer-metal clusters by ion exchange: Polymer-ammonium salts (S₁, S₂) or Polymer-phosphonium salt (S₃) (0.01 mol) was added to the solution of FeCo₃(CO)₁₂ which was prepared by refluxing Co₂(CO)₈ (0.015 mol) and Fe(CO)₅ (0.01 mol) in acetone (50 ml), and the reaction mixture was maintained at 40 °C with stirring for 16 h. Finally the polymer beads were filtered and Soxhlet-extracted with petroleum ether for 20 h, and dried under reduced pressure. They are numbered as I, II, III.

Found: (I) Fe 5.27, Co 15.83, N 2.93, Cl 5.39, C 47.64, H 3.38

(II) Fe 4.47, Co 13.60, N 2.48, Cl 4.57, C 51.04, H 3.38

(III) Fe 2.92, Co 9.30, P 4.04, I 9.94, C 60.48, H 4.37

Preparation of the polymer-phosphine substituted Fe-Co tetrametallic cluster (named as IV): In petroleum ether (bp. 60–90 °C), PS/DVB-CH₂PPh₂ (7.16 mmol P) and PhCH₂NMe₃FeCo₃(CO)₁₂ were refluxed for 10 h. After filtration, the polymer beads were Soxhlet-extracted with petroleum ether for 10 h to remove soluble metal complexes and dried afterwards under reduced pressure for 16 h. A black polymer was obtained.

Found: (IV) Fe 3.25, Co 10.10, P 4.50, Cl 3.97, N 0.82, C 61.8, H 463

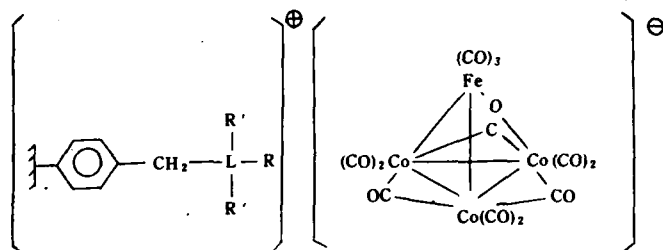
RESULTS AND DISCUSSION

Characterization

The four polymer-supported tetrametallic clusters were prepared by ion exchange (I, II, III) and ligand exchange (IV). Their structures (Scheme 1) were characterized by IR, UV/visible diffuse reflectance spectra and elemental analysis.

In IR spectra, polymer-metal clusters I, II, III and IV showed typical terminal carbonyl absorption frequency at 2000 cm⁻¹ and bridged carbonyl absorption frequency at about 1800 cm⁻¹ (Table 1). Their IR spectra were similar to that of homogenous cluster PhCH₂NMe₃FeCo₃(CO)₁₂. Also, their UV/visible diffuse

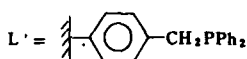
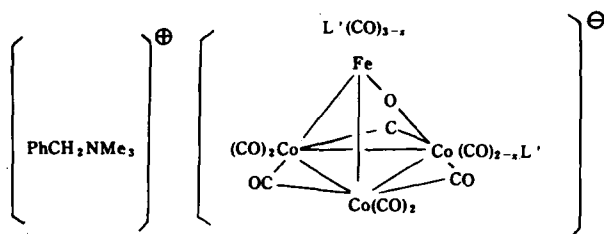
reflectance spectra were similar to the solution absorption spectrum of that homogenous cluster in acetone. All this indicated that Fe-Co tetrametallic cluster was anchored to the polymer supports.



(I) $R = R' = \text{CH}_3$, $L = \text{N}$

(II) $R = \text{Ph}$, $R' = \text{CH}_3$, $L = \text{N}$

(III) $R = \text{CH}_3$, $R' = \text{Ph}$, $L = \text{P}$



(IV)

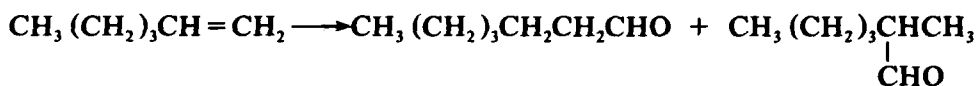
SCHEME 1

Table 1 Spectroscopic results and elemental analysis

Cluster	$\nu_{\text{co}}/\text{cm}^{-1}$			$\lambda \text{ max}/\text{nm}$		Molar ratio Fe : Co
$\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$	2064 m	2000 vs	1986 s	610 (sh)	505	1 : 3
	1974 w	1856 w	1810 s	370		
I	2062 w	2002 vs	1965 m	575 (sh)	500	1 : 2.9
	1925 m	1801 s		380		
II	2062 w	2000 vs	1968 m	580 (sh)	503	1 : 2.9
	1920 m	1810 s		370		
III	2063 w	2000 vs	1966 m	575 (sh)	506	1 : 3.1
	1915 m	1800 s		375		
IV	2023 w	2001 vs	1980 s	579 (sh)	490	1 : 3
	1900 m	1792 s		369		

The molar ratio of Fe/Co from the elemental analyses of I, II, III and IV were 1:2.9, 1:2.9, 1:3.1 and 1:3.0 respectively (Table 1), in accordance with the theoretical ratio 1: 3 approximately. This confirmed the structure of the four polymer-supported clusters.

Catalytic activity in hydroformylation



The hydroformylation of 1-hexene was carried out in 500 ml autoclave, with polymer-metal clusters I-IV as catalysts. Some results are listed in Table 2 and Fig. 1 (a, b). The cluster $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$ has higher activity than cluster $\text{PhCCo}_3(\text{CO})_9$, because of synergistic action between different metals of heteronuclear cluster in the course of catalytic reaction^[10]. Therefore, polymer-supported clusters I-IV were efficient catalysts for hydroformylation reaction. The turnover numbers calculated from the conversion in Table 2 amounted to 832 — 924 in seven hours.

Table 2 Activity of the metal cluster catalysts

Catalyst	Conversion of 1-hexene (%)	Yield of heptyl aldehyde (%)	Product distribution n/i
$\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$	98.2	98.2	0.7
{ $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$ + PPh_3^a	50.2	50.2	1.0
I	89.2	89.2	1.2
II	90.3	90.3	1.3
III	92.4	92.4	1.2
III + PPh_3^a	48.5	48.5	1.6
IV	45.6	45.6	1.8
IV ^b	83.2	83.2	1.0
$\text{PhCCo}_3(\text{CO})_9$	80.8	79.2	0.8
{ $\text{PhCCo}_3(\text{CO})_9$ + PPh_3^a	33.2	33.2	1.1

Condition: catalyst 0.02mmol, 1-hexene 20 mmol, toluene 5 ml, $30 \text{ kg/cm}^2 \text{ H}_2/\text{CO}=1$, 130°C , 7h.

a. PPh_3 0.04 mmol

b. reaction temperature 180°C .

The activity of catalysts I, II, and III was comparable to their homogenous analog $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$. The cation parts have no obvious effect on the activity of the cluster anion (Table 2).

The phosphine either present in catalyst or added to the reaction medium greatly influenced the activity of clusters (Table 2). The polymer-phosphine-cluster IV showed lower activity than the clusters I, II, and III. This implied that the phosphine in catalyst IV may partly saturate the active centers of the cluster. Decreased activity was also observed when adding PPh_3 to the catalytic systems of $\text{PhCCo}_3(\text{CO})_9$, $\text{PhCH}_2\text{NMe}_3\text{FeCo}_3(\text{CO})_{12}$ and III respectively (Table 2). The same results were noticed in our previous studies^[4].

The cluster catalyst IV had low activity at relatively low temperature (130°C), but activity increased with the rise of temperature in the range of $130 - 180^\circ\text{C}$ (Fig. 1a). The yield of 83.2% aldehyde was obtained at 180°C with turnover number of 832. The activity of cluster catalyst I decreased with the reaction temperature was raised to above 160°C though the activity increased with the rise of temperature in the range of $130 - 150^\circ\text{C}$. These indicated that catalyst IV was more stable than catalyst I in the range of $130 - 180^\circ\text{C}$.

In hydroformylation of 1-hexene, n-heptyl aldehyde and 2-methyl hexanal (iso-heptyl aldehyde) were obtained. Sometimes, corresponding alcohols and hexane were produced because of hydrogenation of aldehydes and hexene. When both homogenous and heterogenous Fe-Co tetranuclear clusters were used as catalysts, only aldehydes were produced. In other words, the selectivity was

100 %. The distribution of *n*-heptyl aldehyde and iso-heptyl aldehyde is represented by *n*/*i*. It is found that ratio *n*/*i* were generally higher with polymer-supported

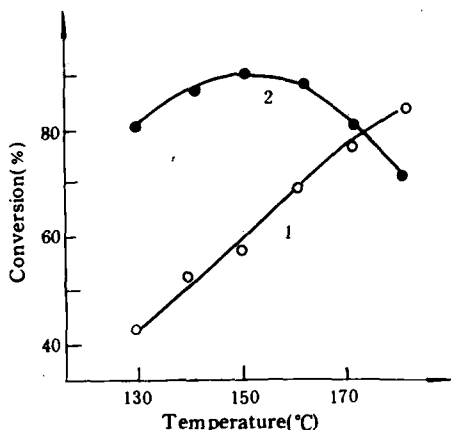


Fig. 1a Effect of temperature on the activity of the clusters (I) and (IV): curve 1, conversion of 1-hexene catalyzed by the cluster (IV); curve 2, conversion of 1-hexene catalyzed by the cluster (I). Conditions: cat. 0.02 mmol, 1-hexene 20mmol, toluene 5 ml, $H_2/CO = 1$, 30 kg/cm², 7h.

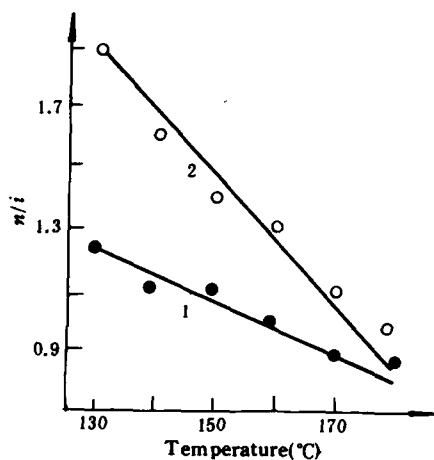


Fig. 1b Effect of temperature on the product distribution (*n*/*i*) in hydroformylation of 1-hexene: curve 1 and 2, *n*/*i* ratio over the clusters (IV) and (I) respectively. Conditions are the same as Fig. 1a.

clusters I-IV as catalysts than that with the cluster $PhCH_2NMe_3FeCo_3(CO)_{12}$ (Table 2). This can be explained by the steric hindrance of the polymer supports. The steric hindrance favours the anti-Markonikoff addition of the catalyst to the olefin. These mean that the polymer-supported cluster catalysts have higher selectivity than the corresponding homogenous cluster catalyst.

We also found that when PPh_3 was added, the ratio *n*/*i* was increased (Table 2). The phosphine may coordinate to the metals of the cluster, thus alter the electronic and steric environments, and eventually influence the ratio *n*/*i*.

With the rise of temperature, the ratio *n*/*i* with both catalyst I and IV decreased (Fig. 1b). Because the mobility of polymer's segments was enhanced by the rise of temperature, the increased mobility did not favour the anti-Markonikoff addition.

Keywords:

Polymer-supported Fe-Co tetrametallic cluster catalyst, hydroformylation of olefin, heterogenous catalysis.

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