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SYNTHESIS OF ANCHORED Rh-Co CLUSTER CATALYSTS AND THEIR HYDROFORMYLATION PROPERTIES

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ABSTRACT

A series of polymer-anchored Rh-Co heteronuclear carbonyl cluster catalysts was synthesized by the reaction of $Co_2Rh_2(CO)_{12}$ with various kinds of polymer supports, such as poly(2-vinylpyridine), poly(*N*-vinyl-2-pyrrolidone), poly(styrene-*co*-maleic anhydride), and aminated products of the latter. The structure of the catalysts was characterized by IR, SEM, XPS, and ICP. The influence of the support structure and crosslinking, the metal content, and the type of substrate on the catalyst's hydroformylation properties was studied. The stability of the catalysts was examined by IR. The experimental results indicate that the supported cluster catalysts possess high catalytic activity, better selectivity, good stability, and reproducibility.

INTRODUCTION

Cluster catalysts have been accorded wide attention by scientists during the past decade [1-15]. Studies of the synthesis and catalytic properties of heteronuclear cluster catalysts are a new trend in the field of Oxo synthesis because the mixed metallic cluster complexes are superior to their monometallic counterparts in their catalytic properties, such as activity, selectivity, stability, and property-regulating possibility. The homogeneous cluster catalysts have many disadvantages, such as instability, difficulty of recovering, and bad reproducibility. On the other hand, the supported catalysts overcome the shortcomings of the homogeneous ones and help in the separation of catalysts from the products. The stability of clusters is greatly enhanced by anchoring on polymers; the catalytic activity and selectivity can be regulated by changing the ligands. In this paper a series of polymeric Rh-Co cluster catalysts supported on poly(2-vinylpyridine) (PVPy), poly(*N*-vinyl-2-pyrrolidone) (PNVP), poly(styrene-*co*-maleic anhydride) (PMAn), and animated products of the latter (APMAn) was synthesized. The catalysts were characterized by many methods and were used to catalyze hydroformylation of olefins. The activity, selectivity, stability, and recycle property of the catalysts were investigated.

EXPERIMENTAL

Reagents

Hexane and pentane (A.R.) were distilled before use, and benzene and toluene (A.R.) were purified by removing thiophene with concentrated sulfuric aicd. 2-Vinylpyridine, styrene, and divinylbenzene were dried several days over anhydrous $CaCl_2$ and distilled before use. The olefins were dried and distilled under nitrogen before use. Other reagents were used as available without any purification.

Catalysts Synthesis

Homogeneous Rh-Co Bimetallic Cluster [16, 17]

The homogeneous tetranuclear cluster $Co_2Rh_2(CO)_{12}$ was prepared according to the reported method [17]:

$$3Co_2(CO)_8 + 2Rh_2(CO)_4Cl_2 \longrightarrow 2Co_2Rh_2(CO)_{12} + 8CO + 2CoCl_2.$$

Synthesis of Polymer Supports

Poly(*N*-vinyl-2-pyrrolidone) (PNVP) [18]

Copolymer beads were prepared by suspension copolymerization of NVP and DVB with AIBN as an initiator. The reaction was carried out at 70°C for 24 h. The beads were filtered off and washed with water, extracted with ethyl alcohol for 6 h, and vacuum dried at 60°C.

Poly(2-vinylpyridine) (PVPy) [19]

The copolymer was prepared by suspension polymerization of styrene, divinylbenzene, and 2-vinylpyridine in the presence of AIBN. The reaction was carried out at 80°C for 1 h, and at 90-92°C for 24 h. The product was washed with methanol to remove the oligomer and extracted with petroleum ether for 4 h, then vacuum dried at 60°C.

Poly(styrene-*co*-maleic Anhydride) (PMAn) [20, 21]

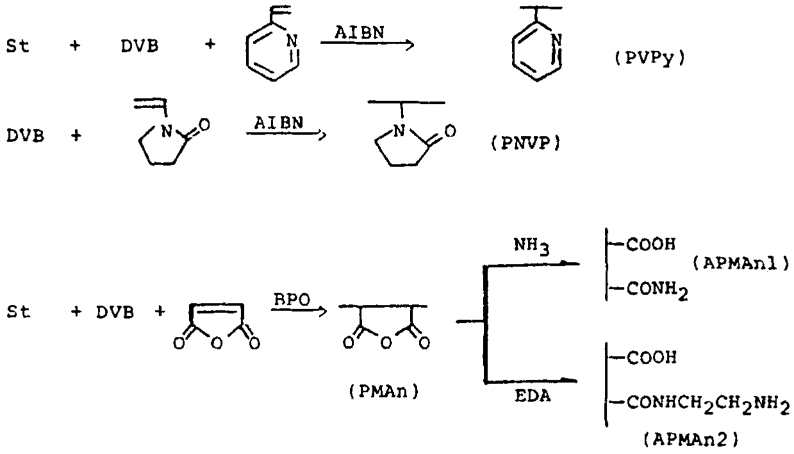
Styrene, divinylbenzene, maleic anhydride, and BPO were mixed. The reaction was carried out by suspension polymerization at 78°C for 4 h, at 85°C for 8 h, at 90°C for 2 h, and at 95°C for 4-6 h. The beads were then filtered and washed, extracted with ethyl alcohol for 6 h, and vacuum dried at 60°C.

The powdery copolymer mentioned above was prepared under nitrogen by precipitation polymerization [22].

Aminated Copolymer of Styrene-Maleic Anhydride (APMAn)

PMAn was reacted with excess ammonia or ethylenediamine for 6 and 40 h, respectively. Then the products were washed with ethanol and dried under vacuum.

The synthesis of the above polymers took place according to Scheme 1.



SCHEME 1. Synthesis of polymer supports.

Synthesis of the Anchored Rh-Co Cluster Catalysts [23-26]

The beads of the polymeric supports, prepared as above, were preswollen in toluene for 2 h at ambient temperature. Then under nitrogen and with continuous stirring, $Co_2Rh_2(CO)_{12}$ was added to the solution. The reaction was carried out at room temperature for 24 h. The products were filtered and washed with absolute alcohol, then dried under vacuum at 60°C.

Characterization of Anchored Catalysts

The IR spectra of the catalysts were recorded with a Nicolet 5DX IR spectrometer. The analysis of the catalysts by scanning electron microanalyzer was carried out with a Hitachi X-650 and the XPS analysis of the catalysts was measured with a Kratos AEI-300 X-ray photoelectron spectrometer. The ICP analysis of the polymeric catalysts was determined by ICAP 9000.

Catalytic Reaction

The hydroformylation reaction was carried out in a 75-mL stainless steel autoclave with a magnetic stirrer. The amounts of olefin, benzene, and catalyst were 5 mL, 15 mL, and 250 mg, respectively. The initial reaction pressure was 55 kg/cm^2; the molar ratio of CO to H_2 was 1.2.

The products were analyzed with an sp-2308 GC (FID detector, 6201 as the carrier and 1,2,3,4-tetracyanoethoxylbutane as the fixed liquid).

RESULTS AND DISCUSSION

Characterization of the Catalysts

IR Spectra

The IR spectrum of $Co_2Rh_2(CO)_{12}$ (Fig. 1) [16] exhibits five characteristic absorptions of carbonyl group (2081.3 (s) cm^{-1}, 2023.0 (s) cm^{-1}, 1906.3 (sh) cm^{-1}, 1874.7 (s) cm^{-1}, and 1847.9 (s) cm^{-1}).

IR spectra of all anchored catalysts show two obvious absorption peaks of carbonyl group within the range of 2000-2100 cm^{-1}. This indicates that there is interaction between the polymeric ligand and the active metals.

Scanning Electron Micrograph

The characterization by SEM indicates that Rh and Co are dispersed homogeneously on the porous supports.

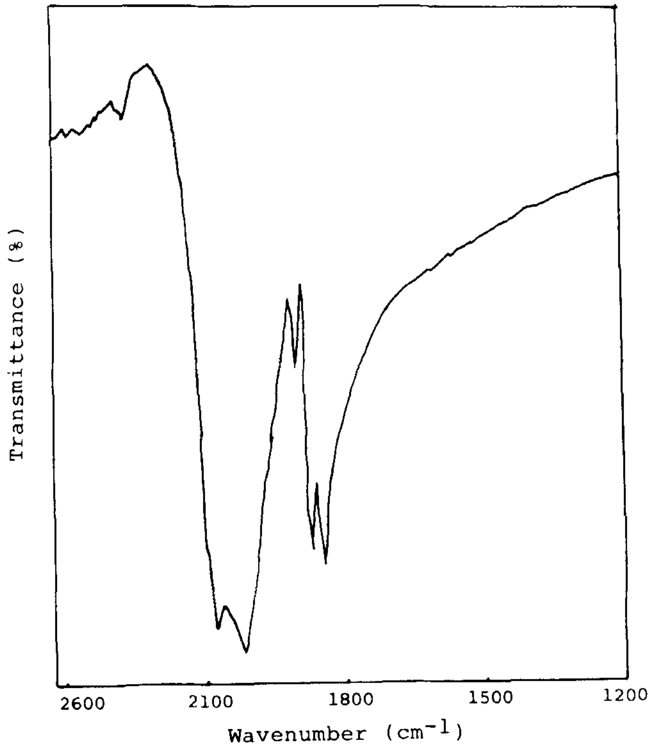


FIG. 1. IR spectrum of $Co_2Rh_2(CO)_{12}$ before use in hydroformylation reaction. ν_{CO} (cm^{-1}): 2081.3 (s); 2023.0 (s); 1906.3 (sh); 1874.7 (s); 1847.9 (s).

XPS Characterization

Homogeneous Cluster. The experimental results show that binding energy (E_b) of $Rh_{3d\ 5/2}$ is 309.6 eV; E_b of carbon and oxygen in carbonyl ligand is C_{1s} = 288.9 eV and O_{1s} = 533.0 eV, respectively. Compared with the spectrum of the standard compound, it indicates that Rh metal corresponds to the rhodium in multinuclear carbonyl cluster; C_{1s} and O_{1s} correspond to the carbonyl of the transition-metal/carbonyl complex.

Anchored Cluster Catalysts. Result of XPS characterization indicates that E_b of N_{1s} and O_{1s} in PNVP support is 399.6 and 531.3 eV, respectively. But E_b of N_{1s} and O_{1s} in the anchored cluster catalyst is

399.5 and 531.5 eV. E_b of O_{1s} is increased by 0.2 eV. The changes show that the O_{1s} donor atom in the anchored cluster possesses more positive property than that of O_{1s} in PNVP support. This may be due to the fact that the electron pair has transferred and the empty d-orbital of rhodium can accept the electrons from the donor atom. Therefore, the p_π-d_π bond was formed. The transfer of a single electron pair of the donor atom (O) leads to a value of E_b of Rh_{3d} in the anchored catalyst lower than that in $Co_2Rh_2(CO)_{12}$. The E_b of $Rh_{3d\ 5/2}$ in the cluster anchored on PNVP is 309.3 eV. However, the E_b of $Rh_{3d\ 5/2}$ in $Co_2Rh_2(CO)_{12}$ is 309.6 eV. The decrease of E_b indicates that there is a weak interaction between the ligand atoms and the active metals. The XPS characterization of the cluster anchored on PMAn showed a decrease of the E_b of Rh_{3d} and an increase in that of O_{1s}.

The Properties of Catalysts

Hydroformylation Properties of Homogeneous $Co_2Rh_2(CO)_{12}$

From Table 1 it can be seen that the activity (conversion) of homogeneous cluster $Co_2Rh_2(CO)_{12}$ is excellent, and that the selectivity for aldehyde is 100%, but its stability is unsatisfactory: it is sensitive to moisture and oxygen, and the separation of catalysts from the reactant is difficult. However, when the homogeneous cluster is anchored on polymer supports, these disadvantages are eliminated.

Hydroformylation Properties of the Polymer-Anchored Rh-Co Cluster Catalysts

It can be seen from Table 2 that the synthesized Rh-Co cluster supported on PNVP, PMAn, APMAn, and PVPy possesses high catalytic activity. The

TABLE 1. The Hydroformylation Properties of $Co_2Rh_2(CO)_{12}$[a]

		Aldehyde selectivity, %		
Catalyst	Conversion, %	Normal	Iso	*n*/*i*
$Co_2Rh_2(CO)_{12}$	96.4	50.0	50.0	1.0

[a] Reaction conditions: 55 kg/cm^2; 80°C; 8 h; H_2/CO = 1.2/1.0; 1-hexene, 5 mL; benzene, 15 mL; catalyst, 9 mg.

TABLE 2. Hydroformylation Properties of the Anchored Co-Rh Bimetallic Catalysts[a]

			Aldehyde selectivity, %		
No.	Support	Conversion, %	Normal	Iso	*n/i*
1	PNVP	95.9	42.7	57.3	0.75
2	PMAn	97.1	46.2	53.2	0.86
3	APMAn1	95.1	38.7	61.3	0.63
4	APMAn2	95.3	36.5	63.5	0.58
5	PVPy[b]	88.1	51.1	48.9	1.05

[a] Reaction conditions as in Table 1. Crosslinking of polymer support, 10%; catalyst, 250 mg.

[b] The percentage of active metals in the catalyst was 1%.

activity of catalysts depends on the kind and strength of the metal-ligand bond (M-L). For PNVP-$Co_2Rh_2(CO)_{11}$ or PMAn-$Co_2Rh_2(CO)_{11}$, the M–CO bond is activated to some extent by the π-acidity of the carbonyl ligand. Therefore, the conjugation of the electrons in the system is increased. In addition, the degree of functionalization of PNVP and PMAn polymer supports is high. All these contribute to the high catalytic activity of the anchored cluster catalyst.

Influence of Crosslinking of the Polymer Support on the Properties of the Anchored Cluster Catalysts

The results in Table 3 show that the polymer-anchored Rh-Co cluster catalysts with different crosslinking possess very high activity, except that of the catalyst PMAn-$Co_2Rh_2(CO)_{11}$ with 2% crosslinking. No alcohol products were found after the reaction. As the crosslinking is increased, the swelling ability of the polymer is decreased. As the pore diameter is decreased, the chance of contact between substrate molecule and catalytic active site is less. This is the reason why the catalytic activity drops. The experimental results show that the type of polymer support backbone exerts a major influence on the catalytic activity. Compared with other crosslinked polymer-supported catalysts, the catalytic activity of PMAn-$Co_2Rh_2(CO)_{11}$ with 2% crosslinking is lower, possibly because the swelling of the 2% crosslinked

TABLE 3. Influence of the Crosslinking of the Support on the Properties of Anchored Rh-Co Cluster Catalysts[a]

Support	Crosslinking, %	Conversion, %	Aldehyde selectivity, % Normal	Aldehyde selectivity, % Iso	*n/i*
PNVP	2	96.4	39.4	60.6	0.65
	6	96.4	43.1	55.6	0.78
	10	95.9	42.7	57.3	0.75
	14	95.8	45.6	54.4	0.84
	20	94.9	43.6	56.4	0.77
PMAn	2	72.3	46.1	53.9	0.86
	6	97.0	44.3	55.7	0.80
	10	97.1	46.2	53.8	0.86
	14	96.4	47.0	53.0	0.81
	20	96.4	41.0	58.9	0.70

[a] Reaction conditions as in Table 1.

TABLE 4. Influence of Bead Size of Polymer Support on the Properties of Catalyst[a]

Bead size	Crosslinking, %	Conversion, %	Aldehyde selectivity, % Normal	Aldehyde selectivity, % Iso	*n/i*
200 mesh (powdery)	10	100	42.0	58.0	0.72
40-60 mesh	10	97.1	46.2	53.8	0.86

[a] Reaction conditions as in Table 1.

PMAn is so high that the concentration of active sites is lower, so that the chance of contact of the olefin with the active components is less.

From the results in Table 4, it can be seen that the bead size of the polymer supports has some influence on the catalytic activity. The smaller beads, which have bigger surface areas, possess higher catalytic activity.

The above discussion shows that PNVP and PMAn are two excellent polymer supports.

Hydroformylation Properties of Rh-Co Cluster Supported on Crosslinked Aminated Poly(styrene-maleic Anhydride) (APMAn)

PMAn polymer can be modified by many kinds of functional reaction, such as amination, acylation, etc. The Rh-Co cluster catalysts anchored on APMAn have high hydroformylation catalytic activity and aldehyde selectivity (see Table 5).

Table 5 shows that the activity of APMAn-$Co_2Rh_2(CO)_{11}$ catalysts is high. The influence of crosslinking on the activity is slight, and the aldehyde selectivity is as high as 100%. APMAn-$Co_2Rh_2(CO)_{11}$ has several positions where coordination can occur. Because of the interaction of the coordination groups, the density of the electron cloud in the system increases, and the M–L bond is activated. In comparison with PAMn-$Co_2Rh_2(CO)_{11}$, the number of functional groups of APMAn-$Co_2Rh_2(CO)_{11}$ increases, and the number of surface-active metals increases also. Thus, the activity of the catalyst is enhanced.

TABLE 5. Hydroformylation Properties of Rh-Co Cluster Catalyst Anchored on APMAn[a]

Support	Crosslinking, %	Conversion, %	Aldehyde selectivity, % Normal	Aldehyde selectivity, % Iso	*n/i*
MAn-St-DVB-NH_2	2	96.0	47.7	52.3	0.71
	6	95.2	43.6	54.4	0.84
	10	95.1	38.7	61.3	0.63
	14	97.1	44.4	55.6	0.80
	20	98.3	45.8	54.2	0.84

[a] Reaction conditions as in Table 1.

TABLE 6. Influence of Content of Active Metals on the Catalytic Behavior of PNVP-$Co_2Rh_2(CO)_{11}$[a]

		Aldehyde selectivity, %		
Content of Rh + Co,[b] %	Conversion, %	Normal	Iso	*n/i*
2.0	94.9	43.6	56.4	0.77
1.66	91.4	47.8	52.2	0.91
1.49	88.4	49.0	51.0	0.96
1.25	85.2	45.5	54.5	0.84
1.10	93.4	50.6	49.4	1.03
0.75	89.2	49.4	50.6	0.98
0.50	88.6	49.0	51.0	0.96

[a] Reaction conditions as in Table 1; crosslinking, 10%.
[b] Determined by ICP.

Influence of the Amount of Active Metals on the Catalytic Properties

In general, as we reduce the amount of active metals in the catalyst, the catalytic efficiency also drops. Hence, we tried to find the optimum conditions for good hydroformylation efficiency at a lower percentage of active metal. The results are shown in Tables 6 and 7.

Table 6 and 7 indicate that activity goes down if the amount of active metals is reduced. However, the effect is not great. Even when the active metal content was 0.5%, the catalytic activity was still high, over 88%, From this, we can conclude that the Rh-Co cluster catalysts anchored on PNVP and PMAn possess very good catalytic properties.

Repeated Use of Catalysts

The lifetime of the anchored catalyst was examined, and the results are shown in Table 8.

The experimental results show that the activity of polymer anchored Rh-Co cluster catalyst remains almost unchanged after use for three cycles, a satisfactory result.

TABLE 7. Influence of Content of Active Metals on the Catalytic Behavior of PMAn-$Co_2Rh_2(CO)_{11}$[a]

		Aldehyde selectivity, %		
Content of Rh + Co, %	Conversion, %	Normal	Iso	*n/i*
2.0	96.4	41.1	58.9	0.70
1.60	92.0	48.7	51.3	0.95
1.45	84.5	47.2	52.8	0.89
1.16	60.0	41.5	58.5	0.71
1.03	93.3	49.4	50.6	0.98
0.70	85.1	47.1	52.9	0.89
0.63	89.5	46.7	53.3	0.88

[a] Reaction conditions as in Table 6.

TABLE 8. Cyclability of Anchored Cluster Catalysts[a]

			Aldehyde selectivity, %		
Support	No. of cycles	Conversion, %	Normal	Iso	*n/i*
PMAn	1	96.4	41.1	58.9	0.70
	2	91.8	37.3	62.7	0.68
	3	89.8	43.6	56.4	0.78
PNVP	1	96.4	41.1	58.9	0.70
	2	92.7	50.8	49.2	1.0
	3	93.9	49.0	51.0	0.96

[a] Reaction conditions as in Table 1; crosslinking of support, 20%

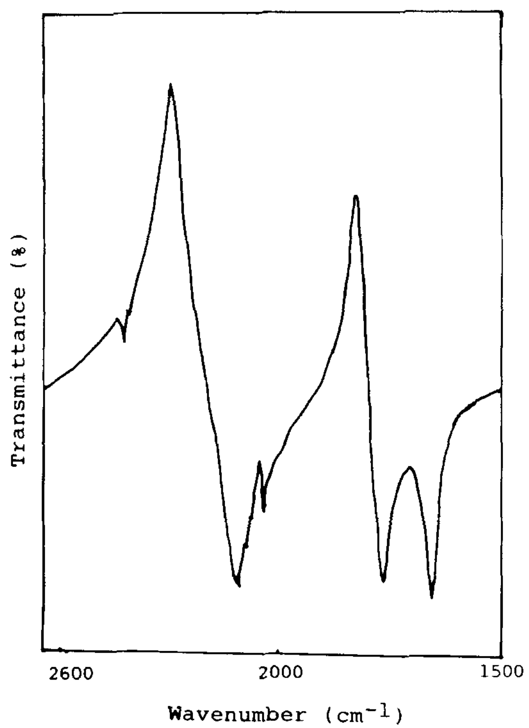


FIG. 2. IR spectrum of $Co_2Rh_2(CO)_{12}$ after use in hydroformylation reaction. ν_{CO} (cm^{-1}): 2073.4 (s); 2017.2 (s); 1799.2 (s); 1707.8 (s).

The Stability of the Catalysts

The structure of $Co_2Rh_2(CO)_{12}$ cluster before and after the hydroformylation was examined by IR in order to evaluate the stability of the catalyst (see Figs. 1 and 2).

From Figs. 1 and 2 it can be seen that the carbonyl absorptions of the cluster catalyst shifted to lower wavenumbers after use in hydroformylation. A possible reason is that $Co_2Rh_2(CO)_{12}$ decomposed to some degree during the reaction. The decomposition may take place as follows:

$$5Co_2Rh_2(CO)_{12} \xrightarrow[\text{Sol.}]{\text{CO}} 2Rh_5(CO)_{15}^- + 4Co^{2+} + 6CO + 6Co(CO)_4^-.$$

TABLE 9. Hydroformylation Properties of PNVP-Supported Catalyst for Different Olefins[a]

	Conversion, %			
Olefin	Experimental	Literature	Product composition, %	
1-Hexene	(95.9)[b]	94.6	Heptanal	
	93.4		Normal, 50.6	Iso, 49.4
Cyclohexene	89.7	58.3	Cyclohexaformaldehyde	Cyclohexylcarbinol
			64.1	35.9
Diisobutylene	76.9	23.7	3,5,5-Trimethylhexanal	100
Styrene	61.4	—	Phenylpropanal	
			Normal, 78.3	Iso, 21.7

[a] Reaction conditions as in Table 1; catalyst, 40-60 mesh; PNVP-$Co_2Rh_2(CO)_{11}$ containing 1% metals.

[b] The percentage of metals was 2%.

The color of the catalyst changed from brown to black during the reaction, suggesting that the structure of the homogeneous cluster had been destroyed.

By examining the IR spectra of anchored clusters before and after the hydroformylation, we found that the characteristic absorption peaks still exist. This indicated that the anchored cluster did not decompose during the reaction. Furthermore, anchored clusters which had been exposed in air for about two months showed no changes observed in the characteristic IR absorptions, indicating very good stability.

Hydroformylation Properties of PNVP-Supported Catalyst for Different Olefins

The results in Table 9 show that the hydroformylation activity and selectivity of the catalyst for various kinds of olefin substrates are high. The order of activity is as follows: hexene-1 > cyclohexene > diisobutylene > styrene. The effect of steric hindrance of the substrates is noticeable. The product of hydroformylation of diisobutylene is 3,5,5-trimethylhexanal, indicating that the hydroformylation site is at the ends of diisobutylene. The catalytic activity of hydroformylation of PNVP-supported catalyst for various olefins is much higher than that reported for other systems [27].

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