

HYDROFORMYLATION CATALYSIS USING POLYMER-SUPPORTED MULTINUCLEAR RHODIUM CARBONYL CLUSTER CATALYSTS*

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ABSTRACT

A series of polymer-supported tetranuclear rhodium carbonyl cluster catalysts were prepared by the reaction of $\text{Rh}_4(\text{CO})_{12}$ with several kinds of polymer supports such as crosslinked poly (N-vinylpyrrolidone) (PNVP) and crosslinked poly (styrene-co-maleic anhydride) (PMAAn)^②, and subsequently were used to catalyze the hydroformylation of olefins. The catalysts were characterized by IR, SEM and XPS. The influence of the supports structure and crosslinking, metal's content and particle size of the supports on the catalysts hydroformylation properties was studied. The factors which affect the catalytic conversion were also examined. The experimental results show that the polymer-supported Rh cluster catalysts possess very high catalytic activity and aldehyde selectivity as well as good reproducibility.

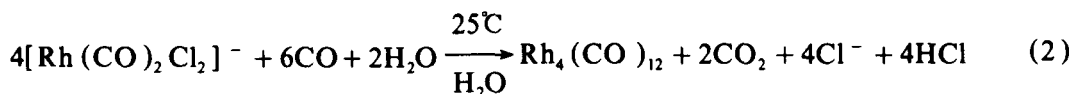
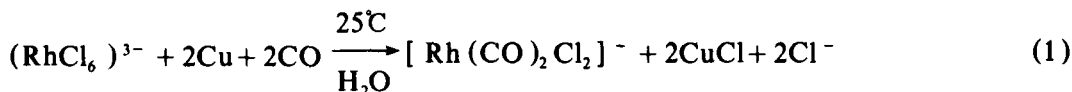
INTRODUCTION

The chemistry and catalysis of metal clusters have become an important new research area during the past decade.^[1-8] The importance is derived from the role of cluster as a bridge between heterogeneous and homogeneous catalysis and it provides an insight into reactions occurring at the surface of metals. In our recent work, we used different polymers as the support for the preparation of catalysts of multinuclear rhodium clusters which were applied for the hydroformylation reaction of 1-hexene. The structures of the catalysts were identified by IR, SEM & XPS and the factors affecting the hydroformylation reactions were determined.

EXPERIMENTAL

Catalysts synthesis

The homogeneous cluster $\text{Rh}_4(\text{CO})_{12}$ was prepared according to the reported method^[9]:



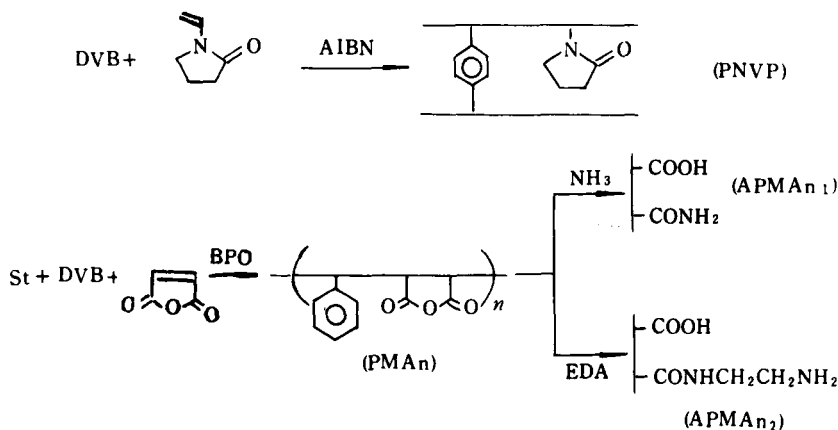
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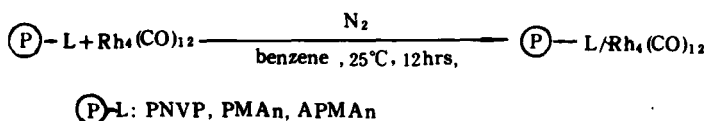
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② Copolymer of styrene and maleic anhydride.

The synthesis of the polymer supports took place according to the following equations: [10]



Polymer-supported tetranuclear rhodium metallic cluster catalysts were synthesized by the reaction of $\text{Rh}_4(\text{CO})_{12}$ with various kinds of polymer supports.



Characterization of the supported catalysts

The IR spectra of the catalysts were recorded with NICOLET 5DX IR spectrometer. The analysis of the catalysts by scanning electron microscope was carried out with HITACHI X-650 and the XPS analysis was made with KRATOS AEI-300 X-ray photoelectron spectrometer.

RESULTS AND DISCUSSION

Characterization of the catalysts

(1). IR spectra

The IR spectra of the anchored catalysts give the obvious characteristic absorption peaks within the range of $1800\text{--}2100\text{ cm}^{-1}$. This indicates that there is interaction between the polymeric ligand and the active metals.

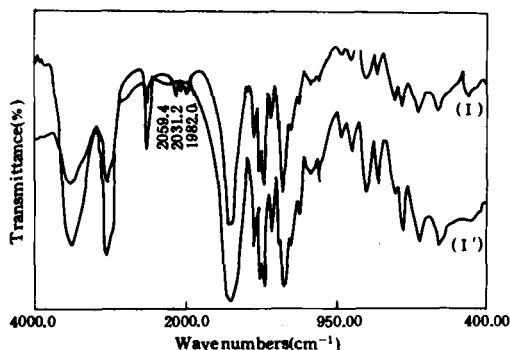


Fig. 1 IR spectra of PNVP/ $\text{Rh}_4(\text{CO})_{12}$ catalyst (I) and the corresponding PNVP support (I')

(2). Scanning electron micrograph

The characterization results of SEM indicate that the Rh active component is dispersed homogeneously on both inner and outer surfaces of porous polymer support.



Fig. 2 SEM of the surface of PNVP support



Fig. 3 SEM of Rh distribution on the surface of PNVP support

(3). XPS characterization

The experimental results are shown in the following table.

Table 1 XPS measurements of the anchored rhodium cluster

Sample	Binding Energy (eV)		
	Rh _{3d 5/2}	O _{1s}	N _{1s}
1. Rh ₄ (CO) ₁₂	309.7	533.7	
2. PNVP/Rh ₄ (CO) ₁₂	308.7	532.3	399.6
3. PNVP		531.3	399.6
4. PMAn/Rh ₄ (CO) ₁₂	308.8	532.5	
5. PMAn		532.2	
6. Linear PNVP/Rh ₄ (CO) ₁₂	309.3	531.9	399.6
7. Linear PNVP		531.4	399.6

It can be seen, from the above table, that the E_b of Rh_{3d5/2} decreases and E_b of donor atom (O_{1s}) in the polymeric ligand increases. This shows that the single pair of electrons have been transferred into the empty 3d orbital of rhodium metal, thus causing the change which confirmed the interaction between the active metal (Rh) and the polymer supports.

The properties of the catalysts

(1) Hydroformylation properties of polymer-supported rhodium cluster catalysts

The comparison of the hydroformylation properties of the supported rhodium cluster catalysts is summarized in Table 2.

Table 2 * Comparison of the properties of the supported rhodium clusters

No.	Support	Conv. (%)	Sel. of Ald. (%)		<i>n</i> / <i>i</i>
			<i>n</i>	<i>i</i>	
1	PNVP	89.1	49.0	51.0	0.96
2	PMA _n	92.1	51.9	48.1	1.08
3	APMA _n ₁	88.7	47.7	52.3	0.91
4	APMA _n ₂	87.4	46.2	53.8	0.36

* Reaction conditions: 55kg/cm², 80 °C, CO/H₂ = 1.2/1.0, 8h.

1-hexene 5ml, benzene 15ml.

Catalyst: 250mg, Rh content: 2%, Crosslinkage of supports: 10%.

From Table 2, it can be seen that all the supported rhodium clusters exhibit good catalytic activity.

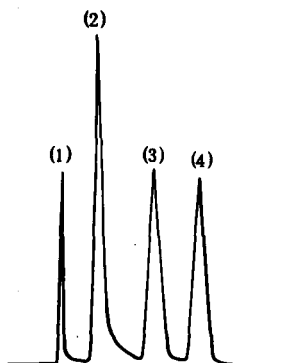


Fig. 4. GC of the product (1) 1-hexene; (2) benzene;
(3) iso-heptaldehyde; (4) n-heptaldehyde

(2) Hydroformylation properties of linear PNVP-supported Rh cluster

Table 3 * Hydroformylation properties of linear PNVP-supported rhodium cluster catalysts

Catalyst	Conversion (%)	Aldehyde	
		Sel. (%)	<i>n</i> / <i>i</i>
Rh ₄ (CO) ₁₂ /PNVP	82.1	100	0.92

* Reaction conditions are the same as those shown in Table 2.

The results in Table 3 show that the linear PNVP-supported Rh cluster catalyst possesses good hydroformylation properties. However, it is inferior to that of the crosslinked PNVP-supported rhodium catalysts (Conv. = 89.1%). This may be due to the fact that either the linear PNVP support's stability is not satisfactory

or its concentration of the active species is not so concentrated as that of the crosslinked supports.

(3) Influence of the amount of active metals on the catalytic properties

The influence of the active metal content (Rh) on the catalytic behaviour of the supported catalysts was also studied, as can be seen in Table 4.

Table 4* Influence of rhodium content on the catalytic behaviour

Support	Active metal content (Rh%)	Conv. (%)	Sel. of Ald. (%)		<i>n</i> / <i>i</i>
			<i>n</i>	<i>i</i>	
PMA _n	2.0	92.1	51.9	48.1	1.10
	1.0	94.6	50.1	49.9	1.00
	0.5	92.8	49.6	50.4	0.99
PNVP	2.0	89.1	49.0	51.0	0.96
	1.0	88.1	50.0	50.0	1.00
	0.5	71.2	49.7	50.3	0.99

* Reaction conditions are the same as in Table 2.

The results in Table 4 indicate that catalytic activity is rather high even if the Rh content of the catalysts is rather low.

(4) The reproducibility of the catalysts

Table 5* Reproducibility of the Supported Rh Cluster Catalysts

Support	No. of reuse	Conv. (%)	Sel. of Ald. (%)		<i>n</i> / <i>i</i>
			<i>n</i>	<i>i</i>	
PMA _n	1	94.9	47.9	52.1	0.92
	2	93.7	44.8	55.2	0.81
	3	93.0	42.4	57.6	0.74
	4	92.4	42.3	57.7	0.73
	5	90.7	40.4	59.6	0.68
PNVP	1	89.0	50.0	50.0	1.00
	2	86.3	49.1	50.9	0.97
	3	84.1	48.5	51.5	0.94
	4	80.3	46.4	53.6	0.87
	5	75.4	46.5	53.5	0.87

* Reaction conditions are the same as in Table 2. Crosslinkage: 20%.

It can be seen, from the Table 5, that the supported rhodium catalysts possess satisfactory recycle properties.

(5) Influence of the crosslinking of the polymer supports on the properties of the anchored cluster catalysts

Table 6 * Influence of the supports' crosslinking on the properties of the anchored catalysts

Support	Crosslinking (%)	Conversion (%)	Aldehyde	
			Sel. (%)	n / i
PNVP	20	86.3	100	0.97
PNVP	10	88.4	100	0.97
PNVP	2	89.1	100	0.96

* Reaction conditions are the same as those shown in Table 2.

The results in Table 6 show that the polymer-supported rhodium cluster catalysts with different crosslinkings possess very high activity. No alcohol products were found after the reaction. As the crosslinking is increased, the catalytic activity becomes lower.

(6) The effect of the particle size on the properties of the supported rhodium catalyst

Table 7 * Influence of the bead size of polymer support on the properties of catalyst

Bead size (mesh.)	Crosslinking (%)	Conversion (%)	Aldehyde	
			Sel. (%)	n / i
200	10	95.9	100	1.0
40 — 60	10	92.1	100	1.1

* Reaction conditions are the same as those listed in Table 2; Catalyst; $\text{Rh}_4(\text{CO})_{12}/\text{PMAAn}$

From the results in Table 7, it can be seen that the beads having bigger surface area possess a higher catalytic activity.

(7) Influence of reaction temperature on the catalytic behavior

Table 8 * The effect of reaction temperature on the properties of the catalyst

Temp. (°C)	Catalyst	Conversion (%)	Aldehyde	
			Sel. (%)	n / i
60	$\text{Rh}_4(\text{CO})_{12}/\text{PNVP}$	96.2	100	1.1
80		93.2	100	1.0
100		92.7	100	1.0

* Reaction conditions are the same as those listed in Table 2.

From the Table 8, we know that the catalytic activity of the anchored rhodium cluster at lower temperature is higher than that at higher temperature, but the influence is not remarkable.

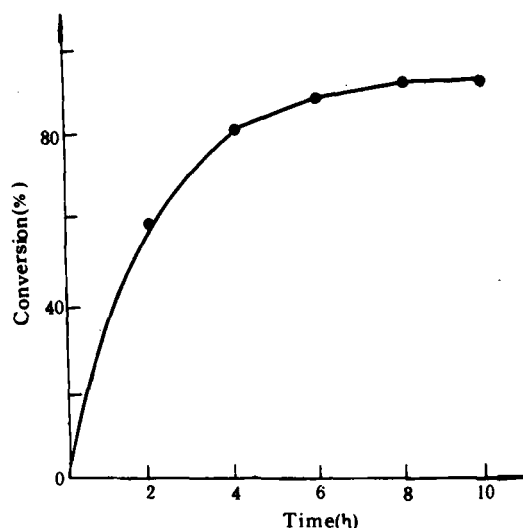
(8) The relationship between reaction time and the properties of the catalyst

From the Table 9, we know that the conversion of the olefins increases with the increasing of reaction time. Within 6 — 8h., most of the substrate has been converted into the product.

Table 9 The effect of reaction time on the catalytic behaviour

Time (h)	Conversion (%)	Aldehyde	
		Sel. (%)	n / i
2	60.7	100	0.39
4	82.8	100	1.0
6	89.0	100	0.96
8	93.0	100	1.0
10	93.3	100	1.1

* Reaction conditions are the same as those in Table 2; Catalyst; PNVP/Rh₄(CO)₁₂

**Fig. 5** The relationship between reaction time and catalytic behaviour**Keywords :**

Rhodium cluster; Polymer catalysts; Hydroformylation

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REFERENCES

- [1] Bradley, J. S.; Hill, E.; Leonowicz, M. E. and Witzke, H., *J. Mol. Catal.*, **1987**, 41, 59.
- [2] Ugo, R. and Psaro, R., *J. Mol. Catal.*, **1983**, 20, 53
- [3] Laine, R. M., *J. Mol. Catal.*, **1983**, 21, 119.
- [4] Tanaka, M. and Saeki K., *J. Organomet. Chem.*, **1987**, 329, 99.
- [5] Gates, B. C., "Metal Cluster in Catalysis", Elsevier Publisher, The Netherlands, **1986**
- [6] Pittman, C. U. Jr.; Honnick W. and Richmond M. G., *J. Mol. Catal.*, **1985**, 32, 177.
- [7] Kagan, Yu. B., *Neftekhimiya*, **1985**, 25 (6), 791.
- [8] Tucci, E. R., *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, 25 (1), 27.
- [9] Martinengo, S.; Chini, P. and Giordano, G., *J. Organomet. Chem.*, **1971**, 27, 389.
- [10] He, B. L.; Sun, J. T.; Li, H. and Sang, J. J., *J. Macromol. Sci.*, **1989**, A26 (2 & 3), 417-431.