

STUDY ON POLYMER—Ru—Co—BIMETALLIC COMPLEXES CATALYSTS I. SYNTHESIS OF CATALYSTS AND THEIR USE FOR THE HYDROFORMYLATION

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ABSTRACT

Six kinds of polymer ligands, supported on SiO_2 , containing coordinating atoms P, S and N respectively, have been synthesized. The Ru(III)-Co(II) bimetallic complexes of these polymer ligands have been obtained and examined as catalysts for the hydroformylation of cyclohexene. The effects of reaction temperature, pressure and Co/Ru ratio etc. on the activities of catalysts were investigated in detail. The catalysts are all polymer-noncarbonyl-metal complexes, easily to be prepared, active and stable. From the experimental results it can be suggested that under reaction conditions such polymer-noncarbonyl-metal complexes convert "in situ" to polymer-carbonyl-metal complexes, thus become active catalysts. The course of this conversion is supposed as a preliminary approach.

INTRODUCTION

In the field of polymer catalysts there are some papers concerned with polymer-bimetallic complexes which were used as polyfunctional catalysts for more than one reaction^[1-3]. Other authors reported polymetallic system for hydroformylation. For example, Hidai et al.^[4] used homogeneous polymetallic system $\text{Co}_2(\text{CO})_8\text{-Ru}_3(\text{CO})_{12}$ and $(\text{Et}_4\text{N})\cdot[\text{FeCO}_3\cdot(\text{CO})_{12}]$ for the hydroformylation of cyclohexene, the reaction rate was twenty seven times faster than that with $\text{Co}_2(\text{CO})_8$. He and coworkers^[5] synthesized polymer-bimetallic catalyst $(\text{RPPH}_2)_2\text{RhCo}_3(\text{CO})_{10}$ (R=Silica) for the hydroformylation of 1-hexene and found that the selectivity of catalyst was improved compared with unsupported one. He^[6,7] and Su^[8] introduced carbonylated Co-Ru cluster into polymer ligands for the purpose to enhance the catalytic activity for the hydroformylation of olefins. Alexander and Knifton^[9] obtained $(\text{P})-(\text{CH}_2)_n\text{PR}_3^+\text{X}^-\cdot\text{RuO}_2\cdot\text{Co}_2(\text{CO})_8$, where (P) represented crosslinked poly(styrene-co-divinylbenzene), polyethylene or poly(methacrylamide), as catalysts for hydroformylation of α -olefins, but in this case the yield of aldehyde was very low (31.6%).

Carbonyl metal complexes are commonly used as the catalyst for the hydroformylation of olefins, but noncarbonyl metal complexes are hardly used till now. In this paper we wish to report the synthetic method of polymer-noncarbonyl-metal complexes and their use as active catalyst for

hydroformylation of cyclohexene. It is suggested that these complexes convert "in situ" to polymer-carbonyl-metal complexes under the reaction conditions and become active catalysts. The effects of polymer ligands and reaction conditions on the catalytic activity were investigated. The mechanism of the conversion of complexes was proposed as a preliminary approach.

EXPERIMENTAL

Materials

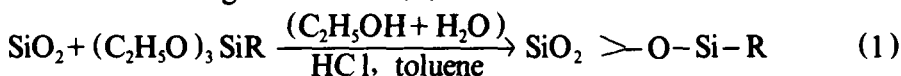
Cyclohexene was treated with ferrous sulfate, washed, dried and distilled under nitrogen. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ slurry contains Ru 30.9 wt%. SiO_2 support is of the specific surface area $380 \text{ m}^2/\text{g}$. Hydrogen and carbon monoxide ($\sim 99\%$) were obtained commercially and used as received.

Analysis and the instruments

IR: Nicolet FT-170 SX. ^1H NMR: Varian EM 360L spectrometer. Gas chromatography: 102G, 103G (Shanghai, China), SE-30 or OV-225 on white support column, thermoconductivity analyzer, toluene as the internal standard.

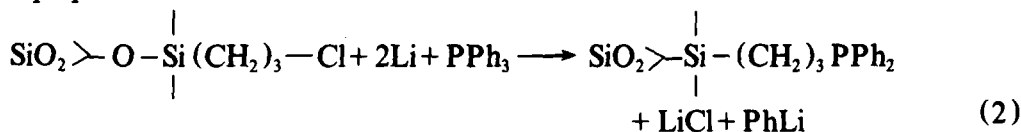
Synthesis of polymer ligands^[10]

Sulfur and nitrogen-containing polymer ligands have been synthesized in the presence of silica according to reaction (1):



Where $\text{R} = -(\text{CH}_2)_3 - \text{Cl}$, $-(\text{CH}_2)_3 - \text{NH}_2$, $-(\text{CH}_2)_3 - \text{NHCH}_2\text{CH}_2\text{NH}_2$,
 $-\text{CH}_2\text{NH---Ph}$, $-(\text{CH}_2)_3 - \text{CN}$, $-(\text{CH}_2)_3 - \text{SH}$

From the polymer ligand with $\text{R} = -(\text{CH}_2)_3 - \text{Cl}$, phosphine-containing ligand has been prepared as shown in reaction (2):



Preparation of polymer-bimetallic complexes

Into a 100 ml flask were placed appropriate amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and absolute ethanol. The mixture was stirred at room temperature till the metal salt dissolved completely. Then water solution of RuCl_3 was added and stirred to get a homogeneous solution. Desired amount of polymer ligand was added and stirring was continued for 2 h. Some drops of concentrated ammonium hydroxide was dripped in, then stirred for another 2h. Complexation was regarded as complete when the upper layer of the reaction mixture turned to clear and colorless. The mixture was filtered and washed with ethanol, dried in the vacuum desiccator, the polymer complexes were obtained as a black-brown powder. The synthetic conditions and results of quantitative analysis of different metal complexes are shown in Table 1 and Table 2 respectively.

Table 1 Synthetic conditions of polymer-bimetallic complexes

No	Ligand ^[10]	Ligand atom : (Co+ Ru) (Mole ratio)	Co : Ru (Mole ratio)	Note
P-1	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 9	5 : 4	
P-2	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	7 : 0	
P-3	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	6 : 1	
P-4	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	5 : 2	
P-5	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	4 : 3	
P-6	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	3 : 4	
P-7	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	2 : 5	
P-8	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	1 : 6	
P-9	SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	12 : 7	0 : 7	
S-1	SiO ₂ >-O-Si- (CH ₂) ₃ SH	12 : 7	4 : 3	
N-1	SiO ₂ >-O-Si- (CH ₂) ₃ NH ₂	12 : 7	4 : 3	
N-2	SiO ₂ >-O-Si- (CH ₂) ₃ NH (CH ₂) ₂ NH ₂	12 : 7	4 : 3	
N-3	SiO ₂ >-O-Si- CH ₂ -NH-Ph ^a	12 : 7	4 : 3	Incomplete complexation
N-4	SiO ₂ >-O-Si- (CH ₂) ₃ CN	12 : 7	4 : 3	

^{a)} Not included in Ref. 10.

Table 2 Quantitative analysis of polymer catalyst

Polymer ligand	Coordinating atom (wt %)	Metal content (wt %) ^a			
		Ru		Co	
		Calc.	Found	Calc.	Found
SiO ₂ >-O-Si- (CH ₂) ₃ PPh ₂	P 5.70				
SiO ₂ >-O-Si- (CH ₂) ₃ SH	S 4.385	3.13	2.84	1.41	1.38 ^{b)}
SiO ₂ >-O-Si- (CH ₂) ₃ NH ₂	N 3.005				
SiO ₂ >-O-Si- (CH ₂) ₃ NHCH ₂ CH ₂ NH ₂	N 3.53				
SiO ₂ >-O-Si- CH ₂ NHPh	N 2.57				
SiO ₂ >-O-Si- (CH ₂) ₃ CN	N 3.86				

a) The metal content of the complexes except the P-SH-(Ru, Co) had not been determined. From this table it is reasonable to believe that the metal content is very close to the calculated value. This demonstrated that the complexation reaction is complete.

b) S : Ru : Co = 12 : 3.5 : 3.5 (mole ratio)

Catalytic hydroformylation of cyclohexene



Into a 25 ml stainless steel pressure bomb were placed appropriate amounts of catalyst, substrate, internal standard toluene and solvent. The bomb was pressurized to the desired pressure with hydrogen and carbon monoxide and heated in a pre-equilibrated oil bath at the proper temperature, stirred with a magnetic stirrer for several hours. Upon completion, the bomb was cooled to room temperature, gases were then vented slowly. The reaction mixture was filtered to separate the catalyst from the reaction solution. The filtrate was analyzed quantitatively by gas chromatography. The catalyst was washed thoroughly with toluene, dried and analyzed by IR spectrophotometer.

RESULTS AND DISCUSSION

Characterization of hydroformylation product

The facts that only the corresponding aldehyde was formed, no side reactions took place which were identified by gas chromatography, indicated that the selectivity to aldehyde of the catalyst is superior to the same type of catalyst.^[9]

The ¹H NMR spectrum of the product cyclohexane-carboxaldehyde is shown as Fig. 1. in which $\delta = 9.4$ ppm is the band of aldehyde H and $\delta = 1-2$ ppm indicates the bands of protons of $-\text{CH}_2-$ and $-\overset{|}{\underset{|}{\text{C}}}-\text{H}$ groups.

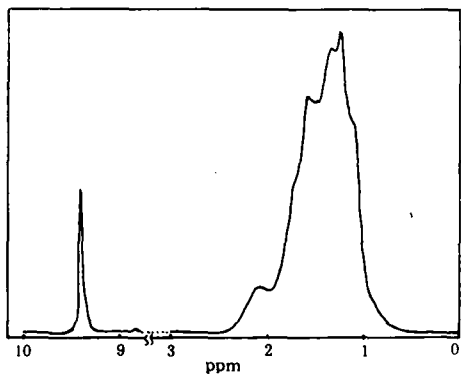
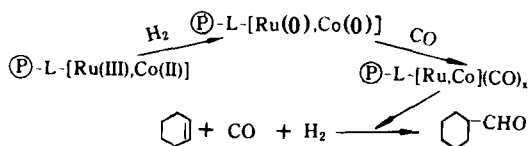


Fig. 1 NMR spectrum of cyclohexane-carboxaldehyde

Characterization of recovered polymer catalyst

Generally noncarbonyl metal complex is inactive for the hydroformylation of olefins, but the synthesized catalysts are just such noncarbonyl metal complexes. Their activity may be attributed to the conversion "in situ" to polymer-carbonyl-complexes in the early stage of reaction, and it is necessary these complexes be reduced to zero valence state before the conversion. The process is proposed as follows:



In the IR spectrum of recovered polymer catalyst (Fig. 2) a peak of high intensity appears at $1900-2100 \text{ cm}^{-1}$. It is well known from the literature^[11-12] that IR characteristic absorption band of carbonyl group in carbonyl-metal complex is present at the region of $1900-2100 \text{ cm}^{-1}$. The result of IR analysis strongly

supports the presence of carbonyl group in recovered catalyst, which means the conversion shown above is very probable.

When the polymer catalyst was treated in THF with H_2 and CO, but without addition of cyclohexene under the same conditons of hydroformylation, the same band appeared in its IR spectrum.

Investigation of various effects on the catalytic activities

1. Influence of Co/Ru ratio on catalytic activity

The compositions of catalysts used are listed in Table 1 (No. P-2 to P-9). The hydroformylation of cyclohexene were carried out under the same conditions and catalyzed by the same amount of metals (Ru+Co). The yield was plotted against the Co/Ru ratio as shown in Fig.3.

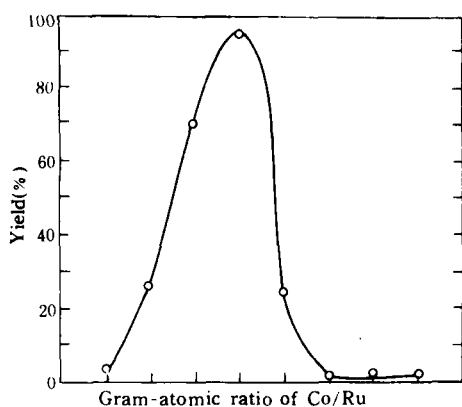


Fig. 3 Relationship between Co/Ru ratio and yield
Conditions: Substrate, cyclohexene, 9.9mmol; catalyst, (Co+Ru), 0.099mmol; P:(Co+Ru) = 12:7; pressure, 60 kg/cm²; CO/H₂ = 1; temperature, 150 °C; reaction time, 24 h.; solvent, THF, 2 ml.

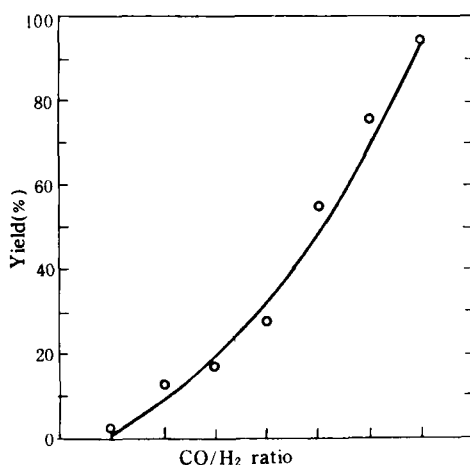


Fig. 4 Relationship between Co/Ru ratio and yield
Conditions: CO/Ru = 6:1. Other conditions as given in Fig. 3.

Fig. 3 indicates that the catalytic activities change markedly with Co/Ru ratio. The complexes containing only one kind of metal (P-2 and P-9) are almost inactive. When the relative contents of Co and Ru are close to each other, the activity increases. A maximum of activity appears as Co/Ru = 4/3 with 95% yield. This fact reveals certain interaction or synergistic effect between Co and Ru of such bimetallic complexes. Possibly it is the interaction that cause the easier conversion of polymer-metal complex to polymer-carbonyl-metal complex in the early stage of reaction. The closer the relative contents of Co and Ru are, the greater the interaction between them, and the more complete the conversion is, so the higher the activity. Here we may find evidence for this idea. It is well known that carbonyl-metal complexes such as $Co_2(CO)_8$ is an active catalyst for the hydroformylation of olefins, however, in our experiments, those complexes with only one kind of metal are almost inactive, which indicates clearly that it is difficult for complexes with only one kind of metal to change to polymer-carbonyl-metal complexes, i.e., interaction between metals is important

for this conversion.

2. Effect of partial pressure hydrogen on the catalytic activity

By keeping the total pressure constant and varying the CO/H_2 ratio in the reaction system from 5:1 to 1:5, the activities of catalysts were greatly changed. Fig. 4 includes the relationship between CO/H_2 ratio and yields of the reactions.

From Fig. 4, the activity of catalysts increase with increasing of H_2 partial pressure. May be the reduction of Ru(III) and Co(II) to Ru(0) and Co(0) takes place easier when the partial pressure of H_2 increases. As a result, the conversion of polymer-metal complexes will be accelerated, the catalysts will be of higher activity.

No cyclohexane was found in the product.

3. Influences of reaction time and temperature on activity of catalyst

The relationships between reaction time, reaction temperature and yields are shown in Fig. 5 and Fig. 6, respectively.

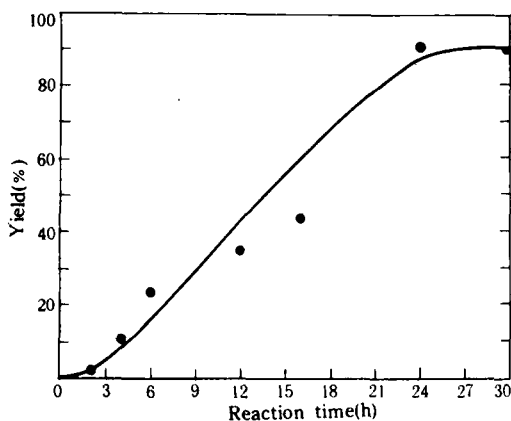


Fig. 5 Relationship between reaction time and yield.
Conditions: $\text{Co}/\text{Ru} = 4:3$. Other conditions as given in Fig. 3

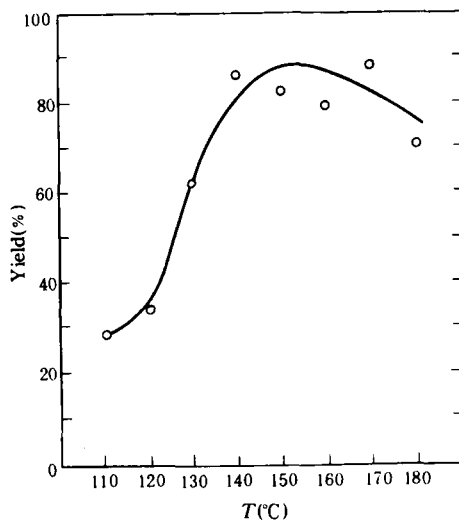


Fig. 6 Relationship between temperature and yield
Conditions as given in Fig. 3

Fig. 5 shows an inductive period which may be caused by the conversion of noncarbonyl-metal complex to carbonyl-metal complex. The activity of catalyst increases with conversion of more and more noncarbonyl-metal complexes to carbonyl-metal complexes. After 25 h, the yield reaches 90%.

Fig. 6 shows that the activity of catalysts increases with increasing of reaction temperature, but decreases when the temperature is higher than 160°C . It is attributed to the aggregation or leaching of central metals, or chemical change of polymer ligand at elevated temperature.

4. Effect of solvent on activity of catalyst

Effect of solvent on activity of catalyst is illustrated in Table 3. Tetrahydrofuran and carbon tetrachloride are good solvent (see Table 3). However, in the case of CCl_4 , metal leaching in the course of reaction can be observed by the dark-brown color of the reaction solution which was similar to the color

of RuCl_3 solution. Thus the best solvent is THF. The yield in benzene is very low (5.2%).

Table 3 Effect of solvent on activity of catalyst^{a)}

Solvent	THF	Dioxane	Acetone	Benzene	CCl_4
Yield (%)	94.9	16.6	14.1	5.2	97.9

^{a)} Conditions: Substrate, cyclohexene 9.9 mmol; catalyst, (Co+Ru) 0.099 mmol; P : Co : Ru = 12 : 4 : 3; pressure, 60 atm. $\text{CO}/\text{H}_2=1$; temperature, 150 °C; reaction time, 24 h; solvent, 2 ml.

According to Gilmont^[13] and Zhang^[14], THF was often used as solvent in the synthesis of carbonyl-metal complexes under atmosphere of low pressure, these authors considered that metal salts were reduced more rapidly than in other solvents. In our experiments the same consideration may be true, the polymer-noncarbonyl-metal complexes are easily reduced and changed to active catalysts in THF, but this conversion process is difficult to be brought about in benzene and other solvents.

5. Influence of free ligand on the activity of catalyst

Different amounts of free ligand triphenylphosphine (PPh_3) were added to the reaction system, containing complex P-5 as the catalyst. The yields of hydroformylation of cyclohexene under these conditions are listed in Table 4.

Table 4 Yields of hydroformylation in the presence of different amounts of PPh_3 ^{a)}

Run	P (in PPh_3) / P (in polymer ligand) (mole ratio)	Yield (%)
1	0	82.3
2	0.5	28.5
3	1	7.7
4	10	0
5	20	0

^{a)} Conditions: Reaction time, 18 h.; solvent, THF 2ml. Other conditions as given in Table 3.

Activity of catalyst decreases markedly in the presence of free ligand PPh_3 , especially when the concentration of PPh_3 is very high, the yield approaches to zero. The reason of deactivation of catalyst is the coordination of free ligand with metals, the vacant orbitals of metals are occupied and the catalyst turns into coordinative saturated state, therefore the "complexation" of the substrate is hindered, as a result the catalyst loses its activity. At the same time the central metal ions can not accomplish their conversion to carbonyl-metal complexes.

6. Catalytic activities for different substrates

Catalyst P-5 was used for hydroformylation of different substrates. The results are collected in Table 5. The activity increases with decreasing of molecular weight of substrates because the smaller molecules of substrates diffuse more rapidly. The steric hindrance of the polymer ligand is also a considerable factor for the complexation of substrates.

The selectivity of P-5 for hydroformylation of olefins is not good as illustrated by the n/b ratio of products (see Table 5).

7. Relationship between the concentration of catalyst and yield of products.

Table 5 Hydroformylation of different substrates catalyzed by polymer complex P-5^{a)}

Run	Substrate	Conversion (%)	<i>n</i> / <i>b</i> ratio	Selectivity of <i>n</i> to <i>b</i> (%)	Pressure drop (kg / cm ²)
1	Cyclohexene	99			9
2	1-Hexene	95	1.15	53.5	7
3	1-Heptene	82	1.51	60.2	7
4	1-Decene	65.9	1.21	54.8	
5	1-Tetradecene ^b				3
6	Allyl alcohol ^b				4

a) Conditions as given in Table 3. Solvent, THF 2 ml.

b) The hydroformylation products were not analyzed because we have not got the standard substances and suitable GC separating column.

Table 6 Relationship between concentration of catalyst and yield^{a)}

Run	Metal / Substrate (mole ratio)	Yield (%)
1	1 / 20 ^{b)}	98.0
2	1 / 100	88.7
3	1 / 200	27.0
4	1 / 300	21.9
5	1 / 400	25.3
6	1 / 500	21.6
7	1 / 1000	12.1
8	0	0

a) Conditions as given in Table 3. Solvent, THF 2 ml.

b) Reaction time 13 h.

Table 6 demonstrates the results of hydroformylation of cyclohexene catalyzed by different amounts of P-5. The yields are high when catalyst : substrate is 1:100, but decrease drastically at the ratio of 1 : 200.

8. Influence of polymer ligand on catalytic activity

P-5, S-1, N-1, N-2, N-3 and N-4 were tested as catalysts for the hydroformylation of cyclohexene respectively for comparing their activities. The results are included in Table 7.

Table 7 Activities of different polymer complexes for hydroformylation of cyclohexene^{a)}

Run	Polymer complex	Coordinating atom	Yield (%)
1	P-5	P	82.3
2	S-1	S	89.8
3	N-1	N	82.4
4	N-2	N	72.3
5	N-3	N	73.0
6	N-4	N	55.4

a) Conditions as given in Table 3. solvent, THF 2 ml.

Sulfur-containing polymer catalyst S-1 is the most active among the catalysts listed above. Moreover, the activities of four kinds of nitrogen-containing polymer complexes are affected by the circumstances surrounding the active central metals.

In conclusion, it is worthy of note one of the advantages of polymer-bimetallic catalyst: the stability of the complex is excellent at room temperature. For example, the activity of catalyst P-5 has not changed at all after standing in the open air for one year, possibly due to no existence of carbonyl-metal in the catalyst. But there still exist some serious problems in such polymer catalysts. One is that, though the stability of original complex is very good, when the noncarbonyl-metal complex turned into carbonyl one after it has been used in hydroformylation reaction, the loss of catalytic activity and metals (Ru and Co) are very critical. These make the reusing properties of the complexes very poor. Another problem is that the structure of the bimetallic complexes are by now not very clear. Further work on these aspects and the mechanism of hydroformylation is in progress.

Keywords:

Polymer catalyst; Bimetallic complex; Cyclohexene; Hydroformylation

Acknowledgement The authors wish to thank both the groups of IR and Elemental analysis of Institute of Chemistry, Academia Sinica, and of University of Science and Technology of China.

REFERENCES

- [1] Carlock, J.T., *U. S. Patent* 4, 189, 448, 1980.
- [2] Batchelder, R.F.; Gates, B.C., and Kuijpers, F.P.J., "Proc. 6th Int. Cong. Catal.", The Chemical Society, London, 1977
- [3] Pittman, C.U., Jr. and Smith, L.R., *J. Am. Chem. Soc.*, 1975, 97, 1749.
- [4] Hidai, M.; Fukuoka, A.; Koyasu, Y. and Uchida, Y., *J. Chem. Soc., Chem. Commun.*, 1984, 516.
- [5] He, Binglin; Sun, Juntan; Li, Hong and Sang, Junjie, Preprints of Tokyo Seminar on Macromolecule-Metal Complexes, 1987, 57.
- [6] He, Binglin; Sun, Juntan; Li, Hong and Teng, Kang, Preprints of China-Japan-U.S.A. Trilateral Seminar on Macromolecule-Metal Complexes, 1985, 105.
- [7] He, Binglin; Sun, Juntan; Li, Hong and Sang, Junjie, Preprints of China-Japan Bilateral Symposium on Utilization of CO and CO₂, 1986, 35.
- [8] Su, Guiqin, Preprints of China-Japan-U. S. A. Symp. Heterog. Catal. Relat. Energy Probl., 1982, B07.
- [10] Zhou, Yanzhu and Jiang, Yingyan, *Polymer Preprints (Japan)*, 1979, 28, 2018.
- [11] Wang, Dianxun; Zhou, Yanzhu and Jiang, Yingyan, 高分子通讯 (*Polym. Commun.*), 1984, 89.
- [12] Yamazaki, H. and Wakatsuki, Y., *Org. Synth. Chem. (Japan)*, 1979, 37, 87.
- [13] Gilmont, P. and Blanchard, A. A., *Inorg. Synth.*, 1946, 2, 238.
- [14a] Zhang, Zhengwen; Wang, Xukun; Wei, Dong; Zhao, Weijun; Zhang, Shuji and Fang, Tingquan, 化学学报 (*Acta Chimica*) 1985, 43, 650.
- [14b] Zhang, Zhengwen; Wang, Xukun; Zhao, Weijun; Zhang, Shuji; Fang, Tingquan and Na, Bin, 化学学报 (*Acta Chimica Sinica*) 1986, 44, 506.