

CATALYTIC BEHAVIOR OF SILICA-SUPPORTED POLY- γ -AMINOPROPYL-SILOXANE-Co-Ru BIMETALLIC COMPLEX FOR THE HYDROFORMYLATION OF CYCLOHEXENE

GUAN Shiyou (关士友), HUANG Meiyu (黄美玉) and JIANG Yingyan (江英彦)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

The cobalt and ruthenium bimetallic complex of poly- γ -amino-propylsiloxane (abbr. as Si-CH₂-Co-Ru) was prepared, and it was found that it can catalyze the hydroformylation of cyclohexene effectively with the conversion amounting to over 90%. Cyclohexanecarboxaldehyde was first formed in the hydroformylation, and then further hydrogenated to form cyclohexanemethanol. The conversion was affected obviously by the Co/Ru ratio. When Co/Ru molar ratio was 100–150, i.e. in the very low content of noble metal Ru, the catalytic activity of Si-NH₂-Co-Ru was also very high. The product composition was affected by CO/H₂ ratio in the reaction gas. Aldehyde can be got high selectively by controlling CO/H₂ ratio. Compared with other catalyst system, the Si-NH₂-Co-Ru catalyst has higher catalytic activity and efficiency with very low Ru/Co ratio. The total turnover number was more than 28800 (based on the amount of ruthenium used).

INTRODUCTION

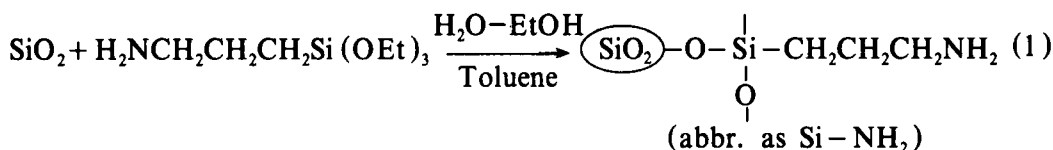
Hydroformylation is a simple way to get aldehyde from olefin. It is a very important process in the chemical industry, especially in the sense of carbon monoxide utilization. It is usually carried out by using the compounds of rhodium as the reaction catalyst. But the use of rhodium compounds is too expensive, thus limiting their application in practice.

A bimetallic system consisting of Co₂(CO)₈ and Ru₃(CO)₁₂ was found to catalyze the hydroformylation of cyclohexene effectively^[1].

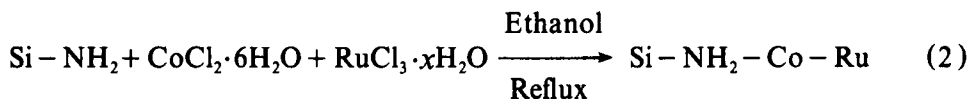
However, the molar ratio of Co/Ru was only about 0.1. That means, relatively large amount of Ru must be used. The turnover number was only 40. In the previous paper, silica-polyalumazane-cobalt-ruthenium complex^[2] could catalyze the hydroformylation of cyclohexene, and the Co/Ru ratio increased to about 0.5. The turnover number amounted to 1300.

Recently, we found that silica-supported poly- γ -aminopropylsiloxane-cobalt-ruthenium bimetallic complex (abbr. as Si-NH₂-Co-Ru) was an effective catalyst for the hydroformylation of cyclohexene, and Co/Ru ratio may be increased to 100–150. The turnover number amounted to 28800. It indicates that Si-NH₂-Co-Ru is very high effective efficiency catalyst. This is very important from the view point of practical application.

EXPERIMENTAL

Preparation of silica supported poly γ aminopropylsiloxane ($\text{Si}-\text{NH}_2$)

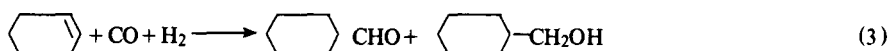
The preparation method of silica-supported poly- γ aminopropylsiloxane was similar to that reported in the previous paper^[3]. For example, toluene (200ml), γ aminopropyltriethoxysilane (10g) and fumed silica (surface area $370\text{m}^2/\text{g}$, 10g) were placed in a flask equipped with a stirrer, a dropping funnel and reflux condenser. After stirring for 10 min., 12 ml of ethanol solution containing 4 ml of water was added dropwise, and the mixture was heated to reflux. During refluxing, the milk white mixture began to approach transparent. After refluxed for 1 hour, toluene and ethanol were distilled off in vacuum. The weight of the product was 15 g. The nitrogen content of the product was 3.29–3.37 wt% (determined by elemental analysis).

Preparation of silica supported poly γ aminopropylsiloxane Co-Ru bimetallic complex ($\text{Si}-\text{NH}_2-\text{Co}-\text{Ru}$)

Several $\text{Si}-\text{NH}_2-\text{Co}-\text{Ru}$ complexes with different Co/Ru ratios were prepared. For example, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2379g, 1mmol) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.0027g, 0.01 mmol) were dissolved in ethanol (15 ml) in a 25 ml flask, and then silica-supported poly- γ aminopropylsiloxane (1.0 g) was added. The mixture was refluxed for about 4 hours until the solution became transparent and colorless and the solid particles turned to light blue (if the Co/Ru ratio of complex is varied, the color of it is somewhat different). After evaporating the solvent, the complexes were dried and ready for use.

The XPS data show that the binding energy of nitrogen in the complexes is higher than that in $\text{Si}-\text{NH}_2$, and the binding energies of metals and chloride in the complexes are lower than those in the corresponding metal chlorides. The XPS peaks of metals in the complexes became broader than those in the metal chlorides. In IR, the absorption bands of $-\text{NH}_2$ at 1570cm^{-1} in $\text{Si}-\text{NH}_2$ shifted to $1600-1620\text{cm}^{-1}$ when the complexes formed. We also observed the bands of N-Ru bond in far-infrared region for $\text{Si}-\text{NH}_2-\text{Ru}$ and $\text{Si}-\text{NH}_2-\text{Co}-\text{Ru}$. All these results confirmed that coordination bonds were formed between metals and nitrogen in the complexes, and the coordination pattern was not single.

Hydroformylation of cyclohexene



Here, CHC stands for cyclohexanecarboxaldehyde and CHM stands for cyclohexanemethanol.

Cyclohexene, Si-NH₂-Co-Ru catalyst and toluene were added to a 100-ml stainless steel autoclave. The autoclave was pressurized with carbon monoxide and hydrogen, and then placed in an oil bath, heated and magnetically stirred for several hours. Upon completion of the reaction, the autoclave was cooled and the gas was vented slowly. The reaction mixture was filtered to separate catalyst. The products were quantitatively analyzed by using gas chromatography.

RESULTS AND DISCUSSION

In order to find suitable reaction conditions for the hydroformylation of cyclohexene, the influence of some important factors was examined. Table 1 shows the influence of Co/Ru molar ratio in the complex on the hydroformylation of cyclohexene. It can be seen that the conversion is affected obviously by the Co/Ru ratio, and the highest conversion is obtained at an optimum ratio. When Co/Ru ratio is in the range of 100-150, that is in the very low content of noble metal Ru, the catalytic activity of Si-NH₂-Co-Ru is still very high. This phenomenon was different from that discovered by Hidai et al.^[1] and Cao et al.^[2] In their papers, the large content of Ru (Co/Ru=0.1-0.5) must be used for getting the higher conversion of cyclohexene.

Table 1 Influence of Co/Ru molar ratio in Si-NH₂-Co-Ru on the hydroformylation of cyclohexene

No.	Co/Ru Molar Ratio	Conversion (%)	Yield of CHC (%)	Yield of CHM (%)
1	0	52.5	11.0	41.5
2	1	63.5	48.9	14.6
3	10	79.9	66.5	13.4
4	50	86.6	85.1	1.5
5	100	90.8	53.2	37.6
6	150	82.6	62.2	20.4
7	200	29.2	29.2	0.0
8	∞	0.0	0.0	0.0

Co+Ru, 0.121 mmol; N/(Co+Ru) mol ratio, 2.53; cyclohexene, 4.8 mmol; solvent, toluene (3.3ml); total pressure, 80kg/cm² (CO/H₂=9/7, at room temperature); 150 °C; 10h.

It also can be seen from Table 1 that Si-NH₂-Co monometallic complex has no catalytic activity and the activity of Si-NH₂-Ru is not high, but Si-NH₂-Co-Ru bimetallic complex has the highest activity at an optimum Co/Ru ratio. These indicate that there is synergistic action between different metals in the bimetallic complex.

In the hydroformylation of cyclohexene, not only CHC but also CHM was produced, because further hydrogenation of CHC would give CHM in higher conversion stage. Further it can be seen from the influence of reaction time on the hydroformylation of cyclohexene (Table 2).

Table 2 Relationship between cyclohexene conversion and reaction time

Reaction time (h)	Conversion (%)	Yield of CHC (%)	Yield of CHM (%)
7	—	—	—
8	60.5	48.4	12.1
10	82.6	62.0	20.6
15	92.1	61.1	30.5

Co + Ru, 0.121 mmol; N/(Co + Ru) mol ratio, 2.53; Co/Ru mol ratio, 150; cyclohexene, 4.8 mmol; solvent, toluene (3.3 ml); total pressure, 80 kg/cm² (Co/H₂ = 9/7, at room temperature)

From Table 2, There was no reaction occurred obviously before 7 hours. That means there is an induction period in the hydroformylation reaction. This phenomenon can

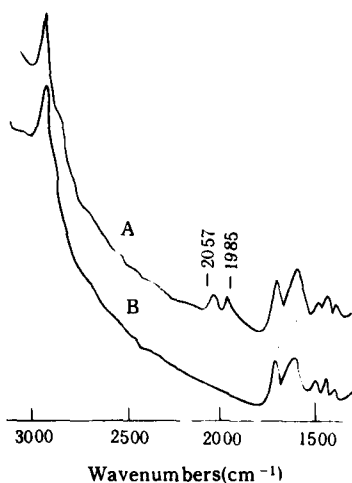


Fig.1 IR Spectra of the Si-NH₂-Co-Ru corresponding to the No.2 in Table 1.

(A) Si-NH₂-Co-Ru

(B) Si-NH₂-Co-Ru after catalytic reaction

be explained by the IR spectra (Fig.1). In the used catalyst which has catalytic activity, there are metal carbonyl absorptions at 1985 and 2057cm⁻¹. It indicated that the carbonylation of metals in Si-NH₂-Co-Ru is taking place to form catalytic active centers during the induction period. When an amount of active centers formed, they catalyze the hydroformylation of cyclohexene synergistically. So after a period of 7 hours, the reaction goes on very fast. The main product is aldehyde. Yield of CHM increases with the increasing of reaction time. This also indicates that the alcohol is coming from the further hydrogenation of the product of aldehyde. The pressure is also an important factor in the hydroformylation reaction catalyzed by Si-NH₂-Co-Ru. Table 3 shows the influence of total pressure. It can be seen that the conversion grows up as the pressures rises in the range of pressure studied, and the increase of total pressure is favorable to the formation of alcohol. At the pressure of 90kg/cm², CHM becomes the main product.

The influence of reaction temperature on the hydroformylation of cyclohexene was also examined. As can be seen in Table 4, the conversion and the yield of CHM go up with the increase of the temperature.

It also can be seen from Table 3 and Table 4 that when the pressure is lower than 60kg/cm² or the temperature is lower than 130 °C, no conversion has been observed. It is assumed that higher pressure and temperature are necessary for the carbonylation of the catalyst itself.

The product composition can be influenced by the CO/H₂ ratio greatly as shown in Table 5.

Table 6 shows the turnover number of Si-NH₂-Co-Ru. It can be seen that the turnover number amounted to 28,800 after 22 hours. Comparing with [1] and [2], the effective catalytic efficiency of Si-NH₂-Co-Ru is very high.

Table 3 Influence of total pressure on the hydroformylation of cyclohexene catalyzed by Si-NH₂-Co-Ru

Total pressure (kg/cm ²)	Conversion (%)	Yield of CHC (%)	Yield of CHM (%)
60	—	—	—
70	82.6	62.0	20.6
80	83.9	49.8	34.1
90	96.0	33.6	62.4

Co+Ru, 0.121 mmol; N/(Co+Ru) mol ratio, 2.53; Co/Ru mol ratio, 150; cyclohexene, 4.8 mmol; solvent, toluene (3.3 ml); CO/H₂ ratio, 9/7; 150°C; 10 h.

Table 4 Influence of reaction temperature

Temperature (°C)	Conversion (%)	Yield of CHC (%)	Yield of CHM (%)
130	—	—	—
140	79.8	68.6	11.2
150	82.6	62.0	20.6
160	81.3	49.7	31.6

Co+Ru, 0.12 mmol; N/(Co+Ru) mol ratio, 2.53; Co/Ru mol ratio, 150; cyclohexene, 4.8 mmol; solvent, toluene (3.3 ml); total pressure, 80 kg/cm² (CO/H₂=9/7, at room temperature); 10 h.

Table 5 Influence of CO/H₂ ratio

CO/H ₂ Ratio (kg/cm ²)	Conversion (%)	Yield of CHC (%)	Yield of CHM (%)
70/10	96.6	93.9	2.7
60/20	90.6	87.8	2.8
50/30	93.5	90.3	3.2
40/40	95.2	85.7	9.5
30/50	95.7	84.1	11.6
20/60	0.0	0.0	0.0

Co+Ru, 0.200 mmol; N/(Co+Ru) mol ratio, 2.53; Co/Ru mol ratio, 100; cyclohexene, 20 mmol; solvent, toluene (10.0 ml); total pressure, 80 kg/cm² (at room temperature); 150°C; 10 h.

Table 6 Turnover number of Si-NH₂-Co-Ru

Reaction Time (h)	Conversion (%)	CHC/CHM (mol ratio)	Turnover Number *
22	96	88/8	28.800

Co+Ru, 0.100 mmol; N/(Co+Ru) mol ratio, 2.53; Co/Ru mol ratio, 100; cyclohexene, 30 mmol; solvent, toluene (15 ml); total pressure, 80 kg/cm² (CO/H₂=1, at room temperature); 150°C.

Keywords:

Cobalt and ruthenium bimetallic complex of poly- γ aminopropylsiloxane catalyst; Cyclohexene; Hydroformylation; Cyclohexanecarboxaldehyde

Acknowledgment The authors acknowledge the support of the National Natural Science Foundation of China.

REFERENCES

- [1] Hidai, M.; Fukuoka, A.; Koyasu, Y. and Uchida, Y., *J. Chem. Soc., Chem. Commun.*, **1984**, 516.
- [2] Cao, S. K.; Huang, M. Y. and Jiang, Y. Y., *Polymer Bulletin*, **1988**, 19, 353.
- [3] Zhou, Y. Z. and Jiang, Y. Y., *J. Organometal. Chem.*, **1983**, 251, 31.