

HYDROFORMYLATION OF MMA CATALYZED BY SILICA-SUPPORTED POLY- γ -AMINO PROPYLSILOXANE- Rh-Co BIMETALLIC COMPLEX

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ABSTRACT

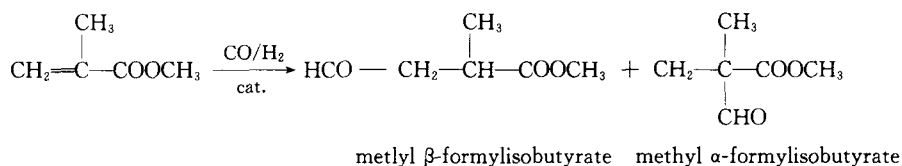
A silica-supported poly- γ -aminopropylsiloxane-rhodium-cobalt bimetallic complex (abbreviated as $\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$) has been prepared and used as catalyst for hydroformylation of methyl methacrylate. The results showed that the catalyst could catalyze the reaction in 95.6% conversion with 92.8% selectivity for the normal aldehyde, methyl β -formylisobutyrate. Such catalyst also showed high stability during the reaction and could be used repeatedly.

INTRODUCTION

Hydroformylation of olefins containing functional groups is not easy as that of simple olefins due to the lower reaction rate and the ease of side-reactions^[1]. Unsaturated esters, especially methyl methacrylate can be hydroformylated to give useful difunctional compounds when catalyzed by rhodium-based catalysts. For example, in presence of 1,2-bis-(diphenylphosphino) ethane, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ could catalyze the reaction to form branched aldehyde with 9.8% selectivity^[2]. A 56% conversion with 98% selectivity for normal aldehyde have also been shown when catalyzed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ ^[3]. Recently, Prokai-Tatrai et al. have found that about 94% yield of normal aldehyde could be obtained when using $\text{Rh}_4(\text{CO})_{12}$ as catalyst for such reaction^[4]. However, the above-mentioned

homogeneous catalysts are not stable during the reaction and difficult to be recovered. In order to overcome these shortcomings, a polymer supported $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was prepared for an attempt, but the catalytic activity was lower than its homogeneous analogue^[3].

Recently, we prepared a silica-supported poly- γ -aminopropylsiloxane-rhodium-cobalt bimetallic complex (abbreviated as $\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$) and it was used as catalyst for the hydroformylation of methyl methacrylate. The results showed that the catalyst could catalyze the reaction with high activity, selectivity and stability.



EXPERIMENTAL

Preparation of silica-supported poly- γ -aminopropylsiloxane

The preparation method of silica — supported poly- γ -aminopropylsiloxane (abbreviated as $\text{SiO}_2\text{-NH}_2$) was similar to that reported in the previous paper^[5]. For example, toluene (200 ml), γ -aminopropyltriethoxysilane (10 ml) and fumed silica (surface area $370 \text{ m}^2/\text{g}$, 10 g) were placed in a flask equipped with a stirrer, a dropping funnel and a 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 refluxing for 1 hour, toluene and ethanol were distilled off under vacuum. The weight of the product was 15 g. The nitrogen content of the product was 3.32 wt%.

Preparation of silica-supported poly- γ -aminopropylsiloxane-rhodium-cobalt bimetallic complex

Silica-supported poly- γ -aminopropylsiloxane-rhodium-cobalt bimetallic complex (abbreviated as $\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$) with different Rh/Co mole ratios were prepared. For example, 0.40 g of $\text{SiO}_2\text{-NH}_2$, 0.040 mmol $\text{RhCl}_3 \cdot \text{H}_2\text{O}$, 0.020 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 15 ml ethanol were placed in the reaction flask equipped with a magnetic stirrer and a reflux condenser. The reaction solution was heated to reflux for 5 hour, after evaporating the solution, the complex was

dried and ready for use. The N/(Rh+Co) and Rh/Co mole ratio in this complex was 16 and 2/1, respectively. XPS analysis of different samples were performed on the PHI 5300 ESCA system (Perkin-Elmer) using an aluminum cathode (1786.6 eV) as the X-ray source.

Hydroformylation of methyl methacrylate

0.5 ml methyl methacrylate, 0.16 g catalyst (containing 0.024 mmol metals) and 3 ml benzene were added to 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 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 gas chromatography using a 2.0 m steel column of SE-30 on silica (80–100 mesh). The products were further characterized by GC/MS coupling (GC: HP-5890, MS: HP-5988). In addition to normal aldehyde, methyl α -formylisobutyrate and iso aldehyde, methyl α -formylisobutyrate, trace amount of by-products were also observed.

RESULTS AND DISCUSSION

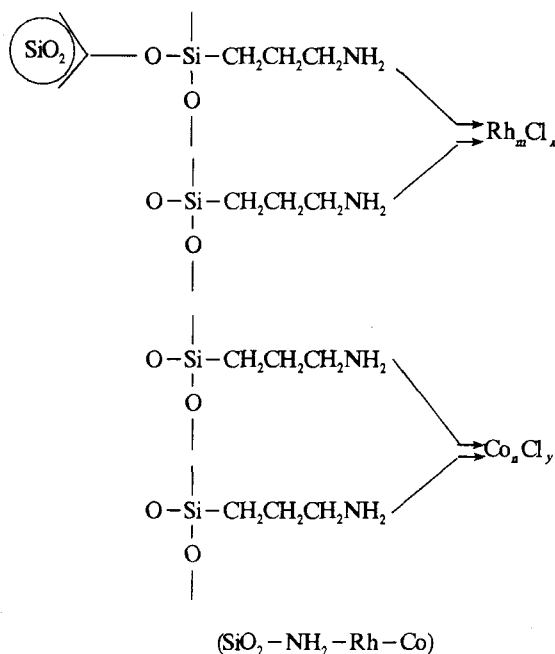
Table 1 shows the X-ray photoelectron spectroscopy (XPS) data for $\text{SiO}_2\text{-NH}_2$, $\text{SiO}_2\text{-NH}_2\text{-Rh}$, $\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$ (at Rh/Co molar ratio of 2/1), RhCl_3 and CoCl_2 . It was found that the binding energies of N_{1s} in the complexes were higher than that in $\text{SiO}_2\text{-NH}_2$, and the binding energies of $\text{Rh}_{3d5/2}$, Co_{2p} and Cl_{2p} in the complexes were lower than those in RhCl_3 and CoCl_2 . However, the binding energies of other atoms showed completely no change before and after complexing. These results showed that coordination bonds were formed between

Table 1 XPS data for $\text{SiO}_2\text{-NH}_2$ and Rh,Co compounds

Sample	Electron binding energy (eV)			
	N_{1s}	$\text{Rh}_{3d5/2}$	Co_{2p}	Cl_{2p}
$\text{SiO}_2\text{-NH}_2$	399.1	—	—	—
$\text{SiO}_2\text{-NH}_2\text{-Rh}$	399.5	308.6	—	197.8
$\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$ (Rh/Co = 2/1)	399.6	308.4	781.2	197.8
RhCl_3	—	309.1	—	198.7
CoCl_2	—	—	781.6	198.8

metal atoms and nitrogen atoms in the complexes. The introducing of Co in the complex had somewhat effect on coordinate state of Rh, i. e., the binding energy of $Rh_{3d5/2}$ would be changed from 308.6 eV in SiO_2-NH_2-Rh to 308.4 eV in $SiO_2-NH_2-Rh-Co$.

The IR spectra showed that the characteristic band of $-NH_2$ shifted from 1570 cm^{-1} in SiO_2-NH_2 to 1630 cm^{-1} in SiO_2-NH_2-Rh and to 1639 cm^{-1} in $SiO_2-NH_2-Rh-Co$, which was due to the accepting part of electrons through coordination with the amino groups of ligand by metallic atoms. These results clearly confirmed the formation of complexes between amino groups in the ligand and metallic atoms. So the structure of $SiO_2-NH_2-Rh-Co$ could be sketched as follows:



The influence of Rh/Co mole ratio in the complex on the hydroformylation of methyl methacrylate was firstly investigated. As it can be seen from Table 2, the conversion and products selectivity were greatly affected by the Rh/Co mole ratio. The highest conversion and the highest yield of normal aldehyde, methyl β -formylisobutyrate were both presented at Rh/Co molar ratio of 2/1, which were both higher than those when catalyzed by SiO_2-NH_2-Rh and SiO_2-NH_2-Co .

monometallic complexes. These results mean that a synergistic action between different metals existed in the bimetallic complex. The product selectivity was different from that when catalyzed by a polymer-supported $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, where branched aldehyde was obtained as the main product^[3].

Table 2 Influence of Rh/Co mole ratio on the hydroformylation of methyl methacrylate

Rh/Co Mole ratio	Conversion (%)	Selectivity (%)	
		Normal aldehyde	Iso aldehyde
∞	82.1	81.3	18.7
2/1	93.4	84.8	15.2
1/1	72.0	81.8	18.2
1/2	65.1	82.4	17.6
1/4	36.3	81.2	18.8
1/8	14.6	66.6	33.4
0	0	—	—

Condition: total amount of Rh and Co, 0.024 mmol; $N/(\text{Rh}+\text{Co})$ mole ratio, 16; methyl methacrylate, 0.5 ml; benzene, 3 ml; total pressure, 80 kg/cm² ($\text{CO}/\text{H}_2=1/1$, at room temperature); 130°C; 12 h

Table 3 shows the influence of temperature on the hydroformylation of methyl methacrylate. It was found that there was no reaction observed at 100°C. With increasing temperature, the conversion and the yield of normal aldehyde both increased accordingly until a highest conversion of 95.6% and a highest normal aldehyde selectivity of 92.8% were obtained at 150°C. Further increasing of the temperature would cause the decrease of conversion and the selectivity of normal aldehyde to a lower value.

Table 3 Influence of temperature on the hydroformylation of methyl methacrylate

Temperature (°C)	Conversion (%)	Selectivity (%)	
		Normal aldehyde	Iso aldehyde
100	0	—	—
110	10.4	66.7	33.3
120	62.4	78.2	21.8
130	93.4	84.8	15.2
140	91.7	81.4	18.6
150	95.6	92.8	7.2
160	70.6	81.5	18.5

Condition: Rh/Co mole ratio, 2/1; others the same as in Table 2

Table 4 shows the influence of $N/(Rh+Co)$ mole ratio in the catalyst on the hydroformylation of methyl methacrylate. It can be found that the $N/(Rh+Co)$ mole ratio had little influence on the conversion, but much influence on the distribution of the products. The yield of normal aldehyde increased with increasing $N/(Rh+Co)$ mole ratio and a highest selectivity for the normal aldehyde could be obtained at $N/(Rh+Co)$ molar of 24. It means that higher content of nitrogen in the catalyst favors the formation of normal aldehyde. However, the yield and the normal selectivity would decrease if $N/(Rh+Co)$ ratio was further increased to 32.

Table 4 Influence of $N/(Rh+Co)$ mole ratio on the hydroformylation of methyl methacrylate

$N/(Rh+Co)$ mole ratio	Conversion (%)	Selectivity (%)	
		Normal aldehyde	Iso aldehyde
6	95.1	77.8	22.2
12	96.4	80.8	19.2
18	95.6	84.6	15.4
24	97.3	91.5	8.5
30	94.3	89.6	10.4

Condition: Rh/Co mole ratio, 2/1; others the same as in Table 2

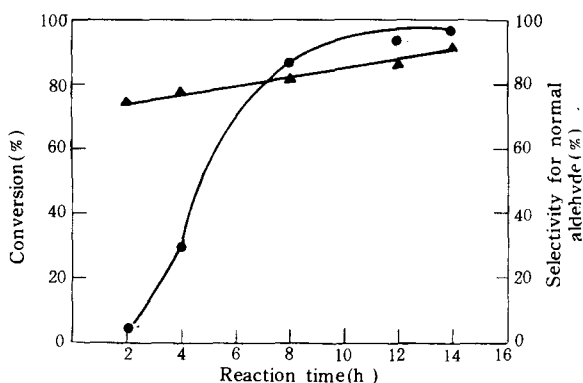


Fig. 1 Influence of reaction time on the hydroformylation of methyl methacrylate catalyzed by $SiO_2-NH_2-Rh-Co$. ● Conversion; ▲ Selectivity for normal aldehyde

Condition: Rh/Co mole ratio, 2/1; others the same as in Table 2

The influence of reaction time on the conversion and normal selectivity was shown in Fig. 1. After 2 hours of induction period, the reaction took place rapidly to reach 100% conversion at 14 hours. A slow isomerization of the branched aldehyde to the normal aldehyde was also observed during the reaction process.

Table 5 shows the stability of the catalyst in recycling experiments. It can be seen that after using the catalyst for three times, the conversion and the products selectivity were both little changed. It means that the catalyst is stable in catalyzing hydroformylation reaction and can be used repeatedly.

Table 5 Stability of $\text{SiO}_2\text{-NH}_2\text{-Rh-Co}$ in hydroformylation of methyl methacrylate

Times of catalyst used	Conversion (%)	Selectivity (%)	
		Normal aldehyde	Iso aldehyde
1 ^a	92.4	83.7	16.3
2 ^b	94.3	82.6	17.4
3 ^c	90.6	84.3	15.7

Condition; Rh/Co mole ratio, 2/1; others the same as Table 2

- a. with fresh catalyst; b. with once-used catalyst;
c. with twice-used catalyst

Keywords:

Silica-supported poly- γ -aminopropylsiloxane; Rhodium-cobalt bimetallic complex; Hydroformylation; Methyl methacrylate

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