Catalytic behavior of silica-supported polyalumazane-Co-Ru bimetallic complex for the hydroformylation of cyclohexene

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Summary

The cobalt and ruthenium bimetallic complex of an inorganic polymer, polyalumazane (abbr. as Al-N-Co-Ru), was prepared. The catalytic behavior of this complex for the hydroformylation of cyclohexene was studied. The conversion percents were more than 90% in a certain reaction temperature and pressure. Both of the conversion and product composition was also affected by the Ru/Co ratio in catalyst and the CO/H_2 ratio in reactant gas. Aldehyde was firstly formed in the hydroformylation, and then it was further hydrogenated to form the corresponding alcohol. There was no any other by-product formed in the reaction. Compared with the corresponding homogeneous catalyst system, the Al-N-Co-Ru catalyst has higher catalytic activity and stability with lower Ru/Co ratio (1.86). After reused for several times, the catalyst did not lose its activity. The total turnover number was more than 2500 (based on the amount of cobalt 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 cobalt carbonyls and the compounds of rhodium as the reaction catalyst. But the cobalt carbonyls are poisonous and usually need rather drastic reaction conditions. In addition, because of the side reactions, higher aldehydes or alcohol yields can not be prepared efficiently. Although the rhodium compounds have higher catalytic activity and higher selectivity for the aldehyde or alcohol formation, the cost of them are too expensive. Therefore, their practical application is fairly limited.

A bimetallic catalyst system consisting of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ was examined to show good catalytic behavior for the hydroformylation of cyclohexene studied by Hidai et al (1). But it is a homogeneous system and the catalyst was not easy to be recovered from the reaction solution and can not be reused. The turnover number was only 400 (based on the amount of cobalt used). And the Ru/Co molar ratio was quite high.

In this paper, we would present a heterogeneous cobalt and ruthenium bimetallic catalyst system for the hydroformylation of cyclohexene. The support used was an inorganic poly-
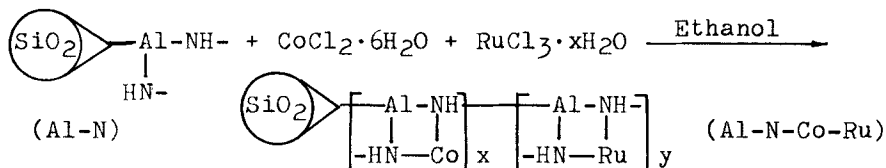
mer, silica-supported polyalumazane.

Experimental

Preparation of Silica-Supported Polyalumazane (Al-N)

See reference (2)

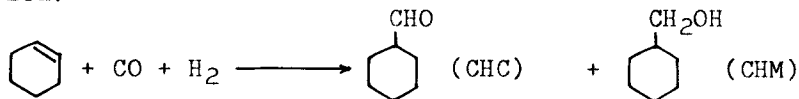### Preparation of Cobalt-Ruthenium Bimetallic Complex of Silica-Supported Polyalumazane (Al-N-Co-Ru)

Reaction:

$$
\text{(SiO}_2\text{)} \text{—Al—NH—} + \text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{RuCl}_3 \cdot x\text{H}_2\text{O} \xrightarrow{\text{Ethanol}}
$$

$$
\overset{\displaystyle \text{HN—}}{\underset{\text{(Al-N)}}{}} \qquad \text{(SiO}_2\text{)} \left[\begin{array}{c} \text{—Al—NH} \\ | \quad | \\ \text{—HN——Co} \end{array} \right]_x \left[\begin{array}{c} \text{—Al—NH—} \\ | \quad | \\ \text{—HN——Ru} \end{array} \right]_y \quad \text{(Al-N-Co-Ru)}
$$

Several Al-N-Co-Ru complexes with different Ru/Co ratio were prepared. For example, $CoCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) and $RuCl_3 \cdot xH_2O$ (1.86 mmol) were dissolved in ethanol (40 ml) in a 100-ml flask, then silica-supported polyalumazane (3.0 g) was added. The mixture was refluxed for about 10 hours untill the solution becomes transparent and colorless and the solid particles become dark grey. After filtered and dried, the cobalt and ruthenium bimetallic complex of silica-supported polyalumazane was ready for use.

Hydroformylation of Cyclohexene

Reaction:

$$
\text{cyclohexene} + \text{CO} + \text{H}_2 \longrightarrow \overset{\text{CHO}}{\bigcirc} \; \text{(CHC)} \quad + \quad \overset{\text{CH}_2\text{OH}}{\bigcirc} \; \text{(CHM)}
$$

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

Cyclohexene, Al-N-Co-Ru catalyst and benzene was added to a 100-ml stainless steel autoclave. The autoclave was pressurized with carbon monoxide and hydrogen, and then placed in a 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 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. It was found that the conversion of cyclohexene was greatly affected by the reaction temperature (Table 1). As the temperature lowered, the conversion was also much lowered. It is assumed that higher reaction temperature is necessary for the carbonylation of the catalyst itself. Three strong absorbed peaks of the carbonyl group appeared on the IR spectrum of the used Al-N-Co-Ru catalyst which shows higher catalytic activity in the hydroformylation of cyclohex-

ene (Fig.2).

Pressure is also an important factor in the hydroformylation reaction catalyzed by Al-N-Co-Ru. Fig.1 shows the relationship between the cyclohexene conversions and reaction pressure. It can be seen that the conversion grows up linearly as the pressure rises in the range of pressure studied.In this series of reactions, a small amount of cyclohexane-methanol(CHM) was also formed in spite of the main product cyclohexanecarbaldehyde(CHC).

Table 1, Influence of Reaction Temperature

Temperature(°C)	Conversion(%)
150	59.1
130	19.5
110	8.8

20 mmol of cyclohexene, 2 ml of benzene, 0.08 mmol of Co, Ru/Co=1.86. 80 kg/cm^2 at room temperature, 10 hours of reaction time. CO/H$_2$=1. A small amount of CHM was formed.

The influence of Ru content in Al-N-Co-Ru catalyst was also examined. As can be seen in Table 2, the conversion of cyclohexene goes up with the increace of the Ru/Co ratio. This phenomenon was similar to that discovered by Hidai et al (1).

In the cases of monometallic systems, the catalytic activity was quite low. This phenomenon can be explained by the IR spectra in Fig.2. In Al-N-Co, there is no carbonyl absorption. In Al-N-Ru, the carbonyl absorptions were quite weak. But in the bimetallic Al-N-Co-Ru system, the carbonyl absorptions were very strong. These findings are taken to indicate that the catalytic active center was the ruthenium carbonyls.

Table 2, Influence of Ruthenium Content in Al-N-Co-Ru

No.	Ru/Co Ratio (mmol)	Yield of CHC (%)	Yield of CHM (%)	Conversion (%)
1	0	7.8	6.1	13.9
2	0.75	35.5	5.0	40.5
3	1.30	55.4	1.2	56.6
4	1.86	56.1	3.0	59.1
5	3.73	4.3	78.7	83.0
6*	∞	21.7	1.2	22.9

20 mmol of cyclohexene, 2 ml of benzene, 0.08 mmol of cobalt, 150°C, 80 kg/cm^2 at room temperature, CO/H$_2$=1, 10 hours.
* The amount of ruthenium used in run 6 was same to that of run 4, but without the use of cobalt.

Fig.1, Influence of Pressure on the Hydroformylation of Cyclohexene Catalyzed by Al-N-Co-Ru.

150°C. For the others, see the legend of Table 1. A small amount of cyclohexanemethanol (CHM) was formed.
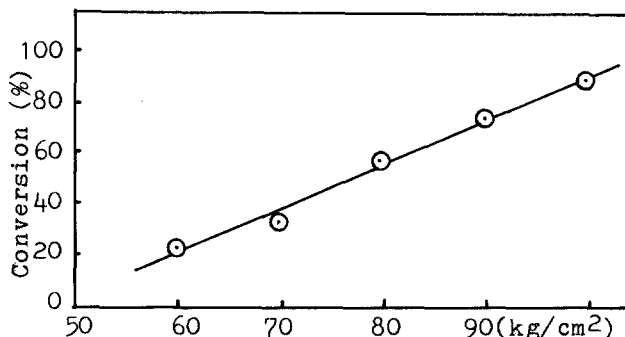
It also can be seen from Table 2 that the main product will be the hydrogenation product if the Ru/Co ratio is big enough. From this point, we can control the composition of the hydroformylation products. The product composition can also be influenced by the CO/H_2 ratio. The results are listed in Table 3.

Table 3, Influence of CO/H_2 Ratio

CO/H_2 Ratio (kg/cm²)	Yield of CHC (%)	Yield of CHM (%)	Conversion (%)
20/70	27.0	12.0	39.0
30/60	2.4	90.9	93.3
40/50	79.5	11.0	90.5
45/45	79.9	10.5	90.4
50/40	37.9	19.6	57.5
60/30	21.8	4.0	25.8
70/20	15.3	5.4	20.7

10 mmol of cyclohexene, 3 ml of benzene, 0.08 mmol of cobalt, Ru/Co=1.86, 150°C, 10 hours of reaction time. Total pressure is 90 kg/cm² at room temperature.
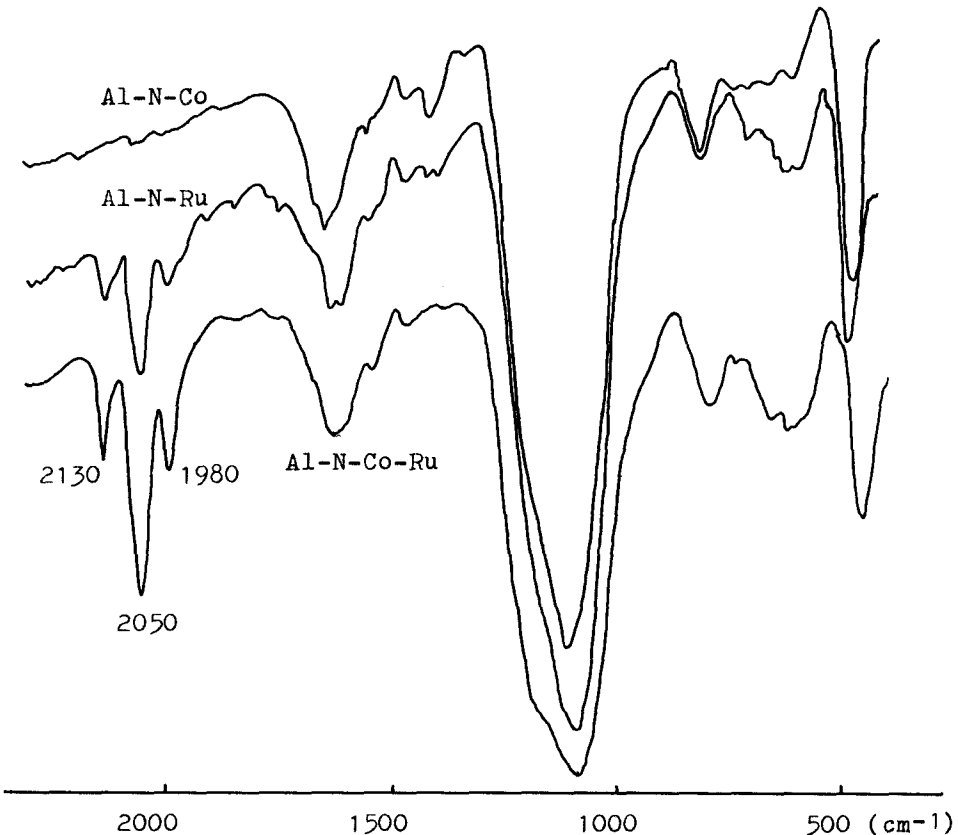

Fig.2, IR Spectra of the Catalysts Used in Table 2, Corresponding to the Runs 1, 4 and 6.

As shown in Table 3, the conversion of cyclohexene was very low when the CO/H_2 ratio was too high or too low and the proper ratio was in a range between 1/2 and 1/1. If we want to get aldehyde rather selectivity, we could choose the 1/1 CO/H_2 ratio, and if the selective production is required, an 1/2 CO/H_2 ratio should be chosen.

The variation of cyclohexene conversion with reaction time is listed in Table 4. At the beginning, the reaction rate is quite slow. This indicates that the carbonylation of the Al-N-Co-Ru catalyst is taking place during the induction period. But four hours later, the reaction goes on very fast. At the eight hours, the main product is aldehyde. But at the ten hours, the main product is changed to alcohol. This also indicates that the alcohol is coming from the further hydrogenation of the product of aldehyde.

Table 4, Relationship between Cyclohexene Conversion and Reaction Time

Reaction Time (hr)	Yield of CHC (%)	Yield of CHM (%)	Conversion (%)
2	15.1	1.9	17.0
4	17.2	1.9	19.1
6	39.4	4.4	43.8
8	84.7	5.2	89.9
10	3.6	89.8	93.4

10 mmol of cyclohexene, 3 ml of benzene, 0.08 mmol of cobalt, Ru/Co=3.73, 150°C, 100 kg/cm^2 at room temperature, CO/H_2=1.

The typical advantage of heterogeneous catalyst is that it can be easily separated from the reaction solution and reused. Table 5 shows that the Al-N-Co-Ru catalyst has no evident loss in catalytic activity after reused for five times. The total turnover number of more than two and a half thousands was achieved.

Table 5, Stability of Al-N-Co-Ru Catalyst

Number of Reusing Times	1	2	3	4	5
Conversion of Cyclohexene(%)	96.8	91.8	92.5	94.6	89.9

20 mmol of cyclohexene for each time, 2 ml of benzene, 0.04 mmol of Co, Ru/Co=1.86, 150°C, CO/H_2=40/50 kg/cm^2 at room T. The reaction time for run 5 was four hours and for the others was ten hours. The product for all runs were aldehyde.

References

1. Hidai, M., Fukuoka, A., Koyasu, Y. and Uchida, Y.: J. Chem. Soc., Chem. Commun., 516 (1984)
2. Yuan, Y.X., Huang, M.Y. and Jiang, Y.Y.: J. Macromol. Sci. -Chem., A24, 261 (1987)