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HYDROFORMYLATION OF HEPTENE-1 CATALYZED BY SOME INORGANIC POLYMER–METAL COMPLEXES

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ABSTRACT

Some inorganic polymers and their complexes with Rh or with Co-Ru were prepared. The catalytic behavior of these complexes for the hydroformylation of heptene-1 was studied. It was found that almost all of the rhodium complexes cannot tolerate higher reaction temperature when higher selectivity is wanted, except for the polyalumazane-Rh complex. But the cobalt and ruthenium bimetallic complex of polyalumazane can catalyze the hydroformylation of heptene-1 at higher temperature without any decrease in catalytic activity and with a selectivity of about 70% for branched aldehyde. Other factors affecting conversion and selectivity were also studied in detail.

INTRODUCTION

Although the hydroformylation of olefins was used industrially as early as the 1940s, there is still wide interest in searching for novel catalysts with high catalytic efficiency. Because of the difficulties in the use of homogeneous catalysts in separation and recovery, considerable effort has been made to "heterogenate" the catalysts, particularly by using polymer supports. Until now, mainly organic polymers have been used, with which the high catalytic activity and selectivity of the homogeneous counterparts can be maintained. For example, polymer-attached $(PPh_3)_3RhH(CO)$ can catalyze the hydroformylation of pentene-1 under rather mild reaction conditions with high aldehyde yield and high normal product selection [1], but the catalytic behavior of transition metals supported on inorganic polymers is still unknown.

A very important feature of immobilized catalysts is that high selectivity can be achieved by choosing the proper support. The chief purpose of this paper is to study the selectivity for inorganic polymer supports.

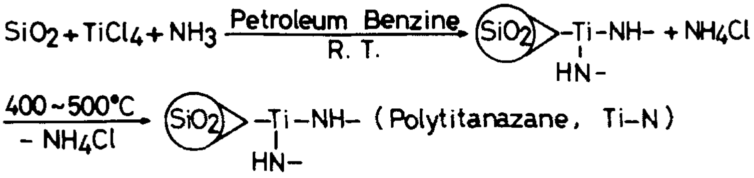
Recently, some new inorganic polymers and their transition-metal complexes were prepared by us. The catalytic behavior of them for hydrogenation [2, 3], isomerization [4], and oxygenation [5] reactions was also studied to some extent. In this paper we present their use in hydroformylation reaction, with heptene-1 as an example.

EXPERIMENTAL

Preparation of Inorganic Polymers

The preparation of polyalumazane (Al-N) and polysilazane (Si-N) is described in Refs. 4 and 5, respectively.

The preparation method of polytitanazane and polystannazane is similar to that of Al-N and Si-N:

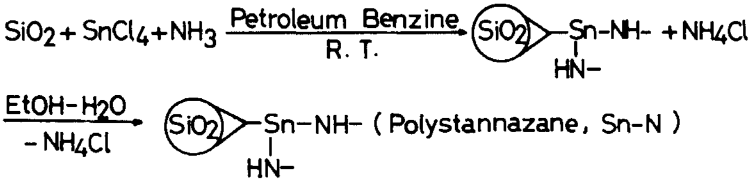


$$SiO_2 + TiCl_4 + NH_3 \xrightarrow[\text{R. T.}]{\text{Petroleum Benzine}} SiO_2\rangle{-}\underset{\underset{\text{HN-}}{|}}{\text{Ti}}{-}NH{-} + NH_4Cl$$

$$\xrightarrow[-\,NH_4Cl]{400\sim500^{\circ}C} SiO_2\rangle{-}\underset{\underset{\text{HN-}}{|}}{\text{Ti}}{-}NH{-} \quad (\text{Polytitanazane, Ti–N})$$

Polytitanazane

Petroleum benzine (500 mL), 40 g titanium tetrachloride, and 20 g fumed silica (surface area 370 m^2/g) were placed in a 1000-mL three-necked flask equipped with a stirrer, a gas inlet tube, and a gas outlet tube. The mixture was stirred, and then ammonia was passed into the flask for about 4 h until the product became alkaline. Since this is an exothermic reaction, the flask had to be cooled by a water bath during the reaction. After filtering and drying, the product was heated at 400-500°C in a furnace to sublime the by-product ammonium chloride. The final product is a fine, light yellow powder.

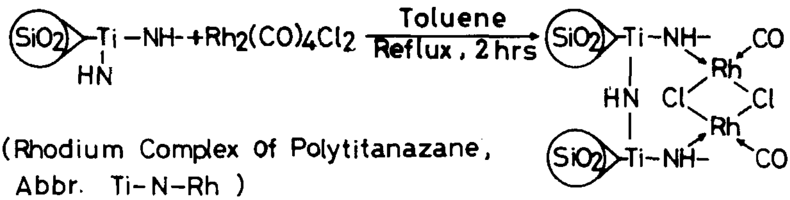


Polystannazane

Preparation was the same as for polytitanazane except for petroleum benzine (400 mL), 13 g stannic chloride, and 5 g fumed silica. The main difference was that the NH_4Cl was removed by washing with a water-ethanol solution.

Preparation of Rhodium Complexes of Inorganic Polymers

$Rh_2(CO)_4Cl_2$ (0.156 g) was dissolved in toluene (30 mL) in a 100-mL flask, then polytitanazane (4.0 g) was added to react with the $Rh_2(CO)_4Cl_2$ for 2 h at 100°C. After filtering and drying, the catalyst was kept in a dessicator, ready for use.



(Rhodium Complex Of Polytitanazane, Abbr. Ti-N-Rh)

The rhodium complexes of other inorganic polymers were prepared by the same method.

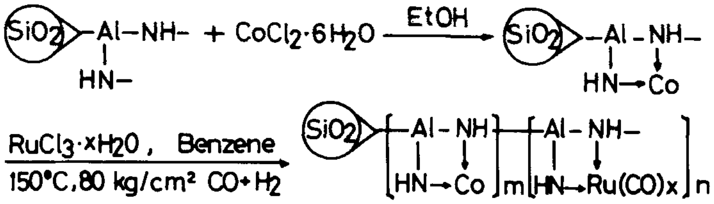
Preparation of Cobalt and Ruthenium Bimetallic Complex of Polyalumazane

$CoCl_2 \cdot 6H_2O$ (0.30 g) was dissolved in ethanol (40 mL) in a 100-mL flask, then polyalumazane was added (3.0 g). The mixture was refluxed for 4 h, then filtered and dried. Consequently, the product was allowed to react with $RuCl_3 \cdot xH_2O$ (0.894 mmol Ru) in 25 mL benzene in a 100-mL autoclave for 10 h at 150°C and 80 kg/cm^2 of a 1:1 mixture of CO and H_2.

TABLE 1. XPS Data for Inorganic Polymers and Their Metal Complexes

	Electron binding energy				
Orbital	Ti-N	Sn-N	Ti-N-Rh	$Rh_2(CO)_4Cl_2$	Al-N-Co-Ru
Ti 2p	459.0		459.0		
N 1s	399.5	400.0	401.4		402.0
Rh 3d5/2			309.7	309.1	
Sn 3d5/2		487.5			
Co 2p					783.0
Ru 3d5/2					283.9

After filtering and drying, the Co-Ru bimetallic complex of polyalumazane (Al-N-Co-Ru) was ready for use.



(Al-N-Co-Ru)

In the IR spectrum of Al-N-Co-Ru, there was only the Ru-CO absorption, but no Co-CO absorption.

The XPS data for Ti-N, Sn-N, Ti-N-Rh, and Al-N-Co-Ru are listed in Table 1.

Hydroformylation of Heptene-1

Heptene-1, catalyst, and benzene were added to a stainless steel autoclave. The autoclave was pressurized with CO and H_2, then placed in a preequilibrated 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 the catalyst. The products were quantitatively analyzed by gas chromatography.

RESULTS AND DISCUSSION

Hydroformylation of Heptene-1 Catalyzed by Rhodium Complexes of Inorganic Polymers

Figures 1 and 2 show results for the hydroformylation of heptene-1 catalyzed by different inorganic polymer-rhodium complexes at different reaction temperatures. It can be seen that the molar ratio of *n*- and isooctyl aldehyde (abbreviated as "*n/i* ratio;" the latter is 2-methylheptanal) decreases as the reaction temperature rises, and for almost all of the rhodium complexes the conversion of heptene-1 also decreases along with increasing temperature, except for Al-N-Rh. The conversion was not affected by reaction temperature. It should be noted that the highest conversion appeared at 80°C for all the rhodium complexes. The conversion was quite low at 60°C, even as low as 30%.

Figure 2 shows that the main product was the isoaldehyde, but for many catalyst systems found in the literature the main product was the *n*-aldehyde (e.g., in Refs. 1 and 6). However, in some cases the iso-product is more useful than the normal one. The above rhodium complexes can be used if more iso-

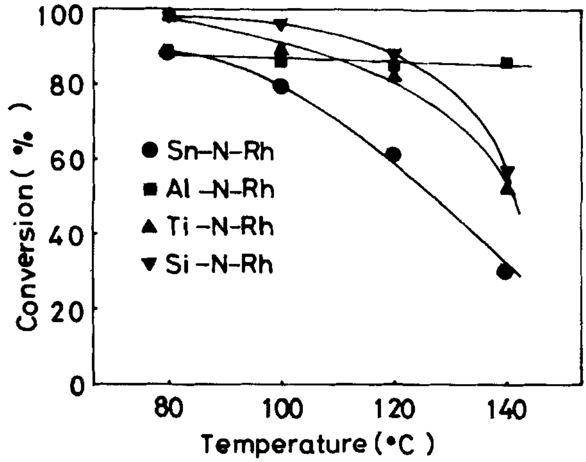


FIG. 1. Hydroformylation conversion of heptene-1 catalyzed by rhodium complexes of different inorganic polymers as a function of temperature. 2 mL heptene-1; 2 mL benzene; 0.01 mmol Rh; 60 kg/cm^2 at room temperature; 8 h reaction time; CO/H_2 = 1.

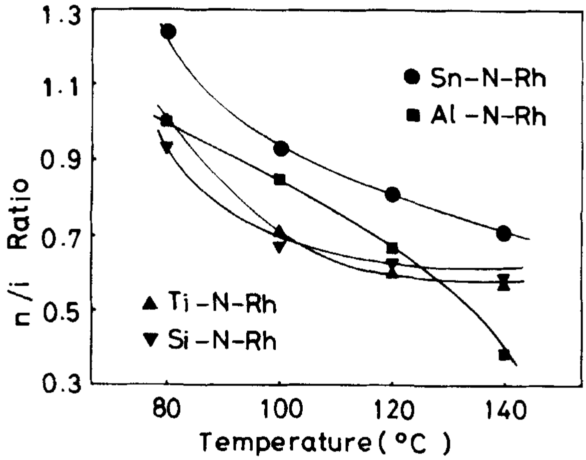


FIG. 2. *n*/*i* Product ratio for the hydroformylations corresponding to Fig. 1. Conditions as in Fig. 1.

product is wanted, but the reaction temperature must be increased, which would lead to reduced conversion. In order to resolve this problem, new catalyst systems were explored (see below).

Hydroformylation of Heptene-1 Catalyzed by the Cobalt-Ruthenium Complex of Polyalumazane

As shown in Fig. 3, the hydroformylation conversion of heptene-1 and the product *n*/*i* ratio are greatly affected by the reaction temperature. Even at 90°C, the conversion of heptene-1 had approached 100%. Thereafter it did not decrease even at 210°C. In this respect the Co-Ru catalyst is quite different from those based on the polymer-Rh complexes discussed above.

The *n*/*i* product ratio decreased nearly linearly with increasing reaction temperature.

The *n*/*i* ratio was also affected by reaction time. Figure 4 shows that the conversion of heptene-1 was above 90% after 6 h. As the reaction time increased, the conversion kept steady while the *n*/*i* ratio continued to decrease gradually. It seems that an isomerization of *n*- to isoaldehyde took place in the hydroformylation process. However, in an experiment under the same reaction conditions as in Fig. 4 with *n*-hexanal as the substrate, we did not find any isohexanal or any other product formed.

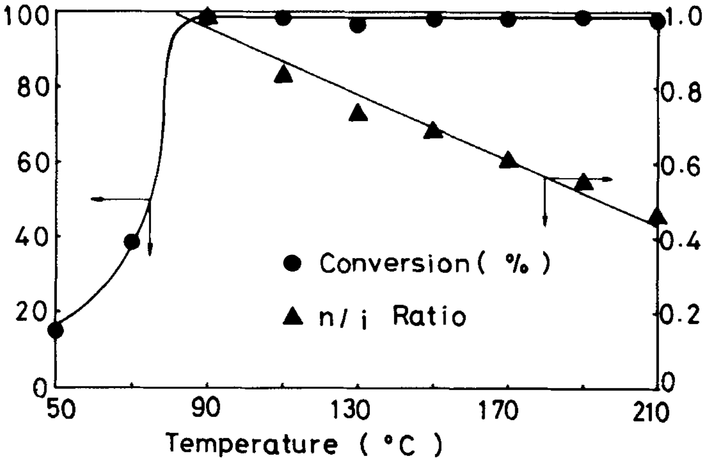


FIG. 3. Hydroformylation of heptene-1 catalyzed by cobalt-ruthenium bimetallic complex of polyalumazane as a function of temperature. 1 mL heptene-1; 3 mL benzene; 0.04 mmol Co; Ru/Co = 1.86; 80 kg/cm^2 at room temperature; CO/H$_2$ = 1; 10 h reaction time.

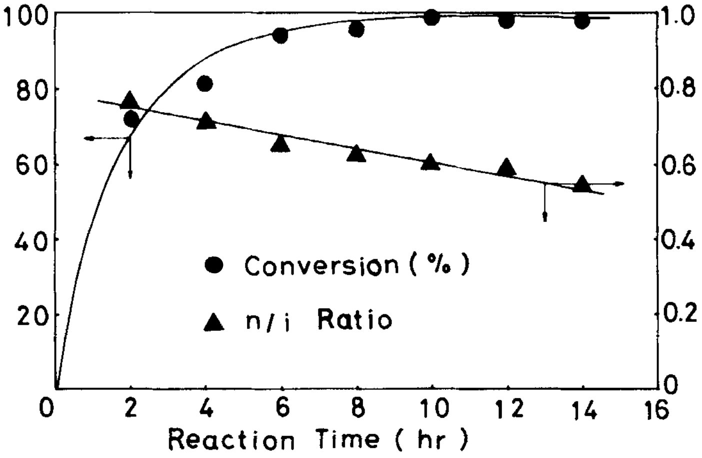


FIG. 4. Influence of reaction time on the hydroformylation of heptene-1 catalyzed by Al-N-Co-Ru. 150°C; 70 kg/cm^2 at room temperature; other conditions as in Fig. 3.

TABLE 2. Influence of CO/H_2 Ratio on Al-N-Co-Ru Catalyzed Hydroformylation of Heptene-1[a]

CO/H_2 ratio, kg/cm^2	Conversion, %	*n*/*i*, mole ratio	Selectivity for iso product, %
40/20	64.7	0.63	61.2
35/25	78.2	0.58	63.5
30/30	97.4	0.68	59.5
25/35	84.5	0.49	67.2
20/40	74.9	0.63	61.2

[a] 1 mL heptene-1, 3 mL benzene, 0.04 mmol Co; Ru/Co = 1.86; 150°C; 10 h reaction time. Total pressure was 60 kg/cm^2 at room temperature.

Table 2 shows that the highest conversion occurs when the CO/H_2 ratio is 1, but the *n*/*i* product ratio does not seem to be affected by the CO/H_2 ratio of unity.

Table 3 shows that the reaction pressure should be at least 60 kg/cm^2 and that the *n*/*i* ratio does not seem to be affected by the pressure.

All the hydroformylation products were aldehydes, i.e., *n*- and isooctyl aldehyde, without any by-products.

TABLE 3. Influence of Pressure on Al-N-Co-Ru Catalyzed Hydroformylation of Heptene-1[a]

Pressure, kg/cm^2	Conversion, %	*n*/*i*, mole ratio	Selectivity for iso product, %
40	61.7	0.54	66.9
50	62.1	0.55	64.4
60	97.4	0.68	59.5
70	99.1	0.59	63.1
80	97.9	0.61	62.1

[a] The pressure was that at room temperature; other conditions as in Table 2; CO/H_2 = 1.

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