

## Catalytic Hydroformylation of Olefins over the Rhodium, Bimetallic Rh-Co, and Cobalt Carbonyl Clusters Supported with Some Metal Oxides

MASARU ICHIKAWA

*Sagami Chemical Research Center, 4-4-1 Nishi-Onuma, Sagami-hara, Kanagawa, Japan*

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Vapor-phase hydroformylation of ethylene and propene proceeded under atmospheric pressure at 25 to 180°C over the Rh and Co carbonyl clusters such as  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ ,  $\text{RhCo}_3(\text{CO})_{12}$ , and  $\text{Co}_4(\text{CO})_{12}$  supported with some specific metal oxides such as ZnO and MgO. It was suggested that the supported carbonyl clusters catalyzed the hydroformylation reactions when they were partially decarbonylated by subjecting to heat treatment *in vacuo* or under hydroformylation atmosphere. The activities and linear-isomer selectivities of aldehyde formation depend not only on the kinds of precursor carbonyl clusters but also on the metal oxides as supporting carriers: The specific activity order at 158°C for Rh carbonyl clusters supported on ZnO was  $\text{Rh}_4(\text{CO})_{12} > \text{Rh}_6(\text{CO})_{16} > \text{Rh}_7(\text{CO})_{16}3\text{NEt}_4 > \text{Rh}_{13}(\text{CO})_{25}\text{H}_{2-3}2\text{NBu}_4$  with a total range of  $\sim 10$ . In contrast, the catalysts prepared from  $\text{Rh}(\text{CO})_2\text{Cp}$ ,  $\text{Rh}_2(\text{CO})_3\text{Cp}_2$ , and  $\text{RhCl}_3$  impregnated on ZnO showed negligible or small conversions in the reactions under similar conditions. The Rh carbonyl clusters were possibly stabilized with the basic oxides such as ZnO, MgO,  $\text{TiO}_2$ , and  $\text{La}_2\text{O}_3$ , exhibiting higher hydroformylation activities. On the other hand, the hydroformylation reactions negligibly proceeded over the carbonyl clusters dispersed on acidic oxides such as alumina, silica-alumina, and  $\text{V}_2\text{O}_5$ . The bimetallic Rh-Co cluster-derived catalysts exhibited higher selectivity of normal-isomer aldehyde, suggesting that Co atoms in the supported bimetallic Rh-Co clusters behave as electronic "donor-ligand" to promote normal-intermediate on top of rhodium atom active for olefin hydroformylation reactions.

### INTRODUCTION

Activities and selectivities of supported metal catalysts are generally influenced with state of metal dispersion and of supporting carriers. In particular, if metal is bimetallic, its electronic properties may be associated with its composition and geometric factors at the surface. The dispersion of metal depends on the systems and procedures of catalyst preparations. Various devices thus have been proposed for highly dispersed metal and bimetallic alloy, for instance, conventional impregnation methods or ion exchange methods (1). In some cases, molecular metallic cluster com-

pounds have been also used as precursors to produce highly dispersed metallic crystallites including bimetallic systems (2). Anderson *et al.* gave a detailed account of this method, and examined the nature of those cluster-derived catalysts (3). It was previously reported by the author that platinum carbonyl cluster-derived catalysts, which were prepared by pyrolysis of  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n 2\text{NEt}_4$  (where  $n = 2, 3, 4$ , and 5) dispersed on  $\gamma\text{-Al}_2\text{O}_3$  or silica gel. The resulting materials catalyzed specifically dehydrocyclization of *n*-hexane under hydrogen atmosphere (4). The dispersed Pt crystallites thus prepared were

supposed of less than 10 Å in size from hydrogen and CO chemisorption stoichiometries (5). It was also reported that supported Rh and Pt carbonyl clusters on some oxides such as MgO, La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> exhibited catalytic activities for methanol (6) and ethanol (7) synthesis from CO and H<sub>2</sub> under atmospheric pressure. The selectivities of oxygenated products markedly depended on the kinds of supporting metal oxides. In this report, our work was extended to the cluster-derived catalysts prepared from Rh, bimetallic Rh-Co, and Co carbonyl clusters in combination with ZnO and other metal oxides, which catalyzed vapor-phase hydroformylation of olefin under atmospheric pressure.

Although hydroformylation reactions readily proceeded in homogeneous systems with monometallic Rh and Co carbonyl complexes, the reactions hardly occurred when those complexes were simply impregnated on silica, alumina, or carbon (8). Recently, Rh and Co exchanged zeolite catalysts have been studied in vapor-phase hydroformylation of olefins under atmospheric or elevated pressures (9). They were reported to have relatively low activity and to produce largely paraffin in hydrogenation. The hydroformylation reaction probably catalyzed by monometallic carbonyl complexes, which were formed on zeolite surface under CO atmosphere (10).

This paper concerns preparations of supported Rh and Co carbonyl cluster catalysts and their catalytic behaviors in olefin hydroformylation reactions. The activities and selective features of the catalysts were studied with varying the compositions of supported carbonyl clusters and metal oxide carriers having different surface properties. Natures of supported carbonyl clusters were also examined by ir spectroscopic measurement and temperature-programmed desorption techniques before and after heat treatment of the

samples *in vacuo* or under hydroformylation atmosphere.

#### EXPERIMENTAL AND PROCEDURES

The catalyst preparation and hydroformylation reaction were carried out in a closed Pyrex glass reactor (total volume was 420 ml), operating in a continuous circulating reaction system. The circulating flow rates of gas were mechanically controlled by the magnetic pumps. Analysis of the reaction products was based on gas chromatography using Porapak Q (4 m, 200°C), polyethylene glycol 1500 (2 m, 80°C) columns for aldehyde and alcohols, and alumina-DMF (38 wt%) (4 m, 25°C) and active Al<sub>2</sub>O<sub>3</sub> (2 m, 0°C) for CO, H<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbons. Highly pure hydrogen, CO, and olefins were used from respective cylinders, after passing a deoxygenation system of reduced copper column and liquid nitrogen trap. Hydroformylation products were separately obtained at the cooling part equipped with dry ice trapping in the circulating reactor.

*Carbonyl cluster compounds.* Rh<sub>4</sub>(CO)<sub>12</sub> was synthesized by the method of Chini and Martinengo (11) and identified by the ir carbonyl absorptions of its hexane solution.  $\nu_{\text{CO}} = 2074, 2069(\text{vs}), 2044, 2041(\text{m}), 1882(\text{s}) \text{ cm}^{-1}$ , Rh<sub>2</sub>( $\pi\text{-C}_5\text{H}_5$ )<sub>2</sub>(CO)<sub>3</sub> was prepared from Rh( $\pi\text{-C}_5\text{H}_5$ )(CO)<sub>2</sub> under prolonged uv illumination (high-pressure Hg lamp) (12). The deep-red crystal was obtained from the crude products in recrystallization, and was identified with Rh<sub>2</sub>( $\pi\text{-C}_5\text{H}_5$ )<sub>2</sub>(CO)<sub>3</sub> from its ir spectra [ $\nu_{\text{CO}} = 2020, 1992(\text{vs}), 1843(\text{s}) \text{ cm}^{-1}$ ] in nujol and solution.  $m/e = 420$  Rh<sub>6</sub>(CO)<sub>16</sub> was purchased from Strem Chem. Co., and used without further purification. Rh<sub>7</sub>(CO)<sub>16</sub>3NEt<sub>4</sub> was synthesized by the method of Martinengo and Chini (13) [ $\nu_{\text{CO}} = 1955(\text{s}), 1770, 1810, 1773(\text{m}) \text{ cm}^{-1}$ ] in acetone solution. Rh<sub>13</sub>(CO)<sub>23</sub>H<sub>2-3</sub>2NBu<sub>4</sub> was prepared by the method of Albano *et al.* (14) in the reaction of Rh<sub>12</sub>(CO)<sub>30</sub>

2NBu<sub>4</sub> under hydrogen atmosphere.  $\nu_{\text{CO}} = 2020(\text{s}), 1840(\text{m}), 1995(\text{s}), 1812(\text{m}) \text{ cm}^{-1}$  in THF. The synthesized carbonyl clusters were stored in a glass ampoule under inert atmosphere. The mixed Rh-Co carbonyl clusters such as  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ , and  $\text{RhCo}_3(\text{CO})_{12}$  were separately prepared in good yields by the method of Martinengo *et al.* (15).  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$  in hexane;  $\nu_{\text{CO}} = 2064(\text{s}), 2060(\text{s}), 1885(\text{s}), 1870(\text{s}) \text{ cm}^{-1}$   $\text{RhCo}_3(\text{CO})_{12}$  in hexane  $\nu_{\text{CO}} = 2050(\text{s}), 2035(\text{m}), 1880(\text{s}), 1855(\text{s}) \text{ cm}^{-1}$   $\text{Co}_4(\text{CO})_{12}$  was obtained quantitatively by the reflux of toluene solution of  $\text{Co}_2(\text{CO})_8$ .

*General procedures of catalyst preparation.* Each carbonyl cluster was deposited from the organic solution (with varying the degree of dispersion) onto metal oxides such as ZnO, MgO, La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, silica, and alumina powders. The organic solvents were carefully removed by vacuum evaporation. The resulting materials were charged in a reactor, and subjected to heat treatments. The entire procedure was performed in a vacuum or under inert atmosphere of He and N<sub>2</sub>, since most of the carbonyl clusters are comparatively air sensitive. The infrared spectra of the carbonyl clusters dispersed on metal oxides were recorded in the range of 2200 to 1600  $\text{cm}^{-1}$  with a Hitachi EPI-G3 grating spectrometer.

## RESULTS AND DISCUSSION

### *Activation of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ Supported on ZnO for Hydroformylation Reactions*

A mixture gas of C<sub>2</sub>H<sub>4</sub> (or C<sub>3</sub>H<sub>6</sub>), CO, and H<sub>2</sub> (1:1:1 molar ratio under total pressure of 65 cm Hg) was admitted onto the supported  $\text{Rh}_4(\text{CO})_{12}$  (0.10 g, 0.12 mmole) or  $\text{Rh}_6(\text{CO})_{16}$  (0.12 g, 0.12 mmole) on ZnO powder (20 g of Kadox 25 ZnO, New Jersey Co., ca. 20 m<sup>2</sup>/g). They were catalytically inactive for the hydroformylation reaction at lower temperatures below 90°C. By raising the temperature above

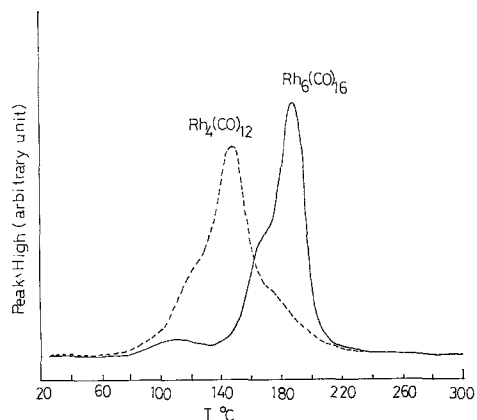


FIG. 1. Patterns of temperature-programmed CO evolution of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  supported on ZnO (0.5 Rh wt% loading). Carrier: He 1 atm, 100 ml/min. Programmed rate of temperature elevation: 5°C/min. The condensed substances were removed at the liquid N<sub>2</sub> trap from the effluent gas. CO was detected by TCD-gas chromatography using AC 1 m column at 25°C.

90°C, the corresponding aldehyde was first produced at the cooling part of the circulating reactor after some induction period (1–2 hr). It was observed volumetrically that additional amounts of CO evolved during the induction period, probably due to the decomposition of the supported carbonyl clusters. This induction period was considerably shortened by elevating the temperatures above 100°C, prior to contact with hydroformylation gas. Evolution of CO was measured by temperature-programmed desorption technique using gas chromatography with active Carbon 1 m column. As shown in Fig. 1, removal of CO from  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  dispersed on ZnO proceeded under helium or hydrogen flow (1 atm, 100 ml/min) at the different temperature ranges of 100 to 145 and 160 to 190°C, respectively. After the stationary state of the hydroformylation reaction was realized, the rates and normal-isomer selectivities of aldehyde formation were reproducibly observed at 25 to 160°C over each resulting catalyst. The aldehyde

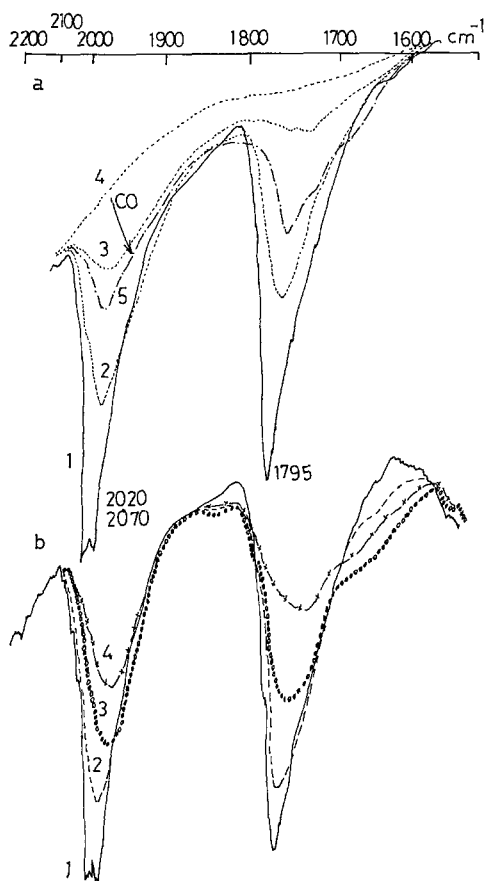


FIG. 2. (a) ir spectral change of carbonyl bands in  $\text{Rh}_6(\text{CO})_{16}$  dispersed on  $\text{ZnO}$  (Kadx 25) before and after heat treatment. (1) Starting sample at 25°C; (2) evacuation for 10 min at 125°C; (3) evacuation for 20 min at 125°C; (4) evacuation for 4 hr at 125°C; (5) readmission of 10 cm Hg of CO onto the resulting material at 25°C. (b) ir spectral change of carbonyl bands in  $\text{Rh}_6(\text{CO})_{16}$  supported on  $\text{ZnO}$  (0.75 Rh wt%) by subjecting to heat treatment under the hydroformylation atmosphere of  $\text{C}_2\text{H}_4$  (15 cm Hg), CO (15 cm Hg), and  $\text{H}_2$  (15 cm Hg). (1) Starting sample at 25°C (—); (2) 90°C in 2.5 hr (---); (3) 100°C in 4.5 hr (•••••); (4) 110°C in 14 hr (—×—×—).

formation obeyed approximately the first-order kinetics in each run.

#### Supported Rh Carbonyl Clusters under Hydroformylation Atmosphere

The infrared spectra of  $\text{Rh}_6(\text{CO})_{16}$  dispersed on  $\text{ZnO}$  (1.5 Rh wt% loading)

recorded in the region of 2200 to 1600  $\text{cm}^{-1}$  before and after subjecting to heat treatment *in vacuo* or under hydroformylation atmosphere. The sample disk (20 mm diameter) was prepared by pressing about 100 mg of the supported material under nitrogen. As shown in Fig. 2a, the ir spectra of the fresh sample gave strong bands at 2020, 2070 (twin), and 1795  $\text{cm}^{-1}$ , which were assigned to the terminal and three-centered bridging carbonyl absorptions, respectively, of  $\text{Rh}_6(\text{CO})_{16}$  in solution and in nujol-mud (11). When the disk sample was evacuated ( $10^{-3}$  Torr) with slowly elevating temperatures up to 150°C, both carbonyl bands parallelly diminished and almost completely disappeared in 1 hr, probably due to evolution of CO. After removal of CO by evacuation, when the pyrolyzed catalyst was exposed to 5 to 20 cm Hg of CO at 25°C, relatively broad bands with about half the intensity of those observed with the starting sample reappeared in the 1985 and 1780  $\text{cm}^{-1}$  regions. The resulting carbonyl bands retained under the hydroformylation gas of  $\text{C}_2\text{H}_4$ , CO, and  $\text{H}_2$  (1:1:1 total pressure of 60 cm Hg) at the elevated temperatures of 100 to 160°C, and it was found that propionaldehyde was formed in the ir cell. Under a mixture of  $\text{C}_2\text{H}_4$ , CO, and  $\text{H}_2$  (molar ratio 1:1:1, 45 cm Hg) the characteristic carbonyl bands of  $\text{ZnO}$ -supported  $\text{Rh}_6(\text{CO})_{16}$  shifted to 1985 and 1785  $\text{cm}^{-1}$  and a weak new band appeared at 1650  $\text{cm}^{-1}$ . The intensities of these bands decreased to half their initial value upon raising the temperature above 110°C, as shown in Fig. 2b. When propionaldehyde was catalytically produced in the ir cell, the carbonyl absorption spectra resembled those of  $\text{Rh}_6(\text{CO})_{15}^{2-}$  and  $\text{Rh}_6(\text{CO})_{14}^{4-}$  or  $\text{Rh}_6(\text{CO})_{15}(\text{COOC}_2\text{H}_5)^-$  in solution, which has been reported by Martinengo and Chini (13). These results suggest that the dispersed Rh crystallites on  $\text{ZnO}$  prepared by pyrolysis *in vacuo* may reconstruct to form

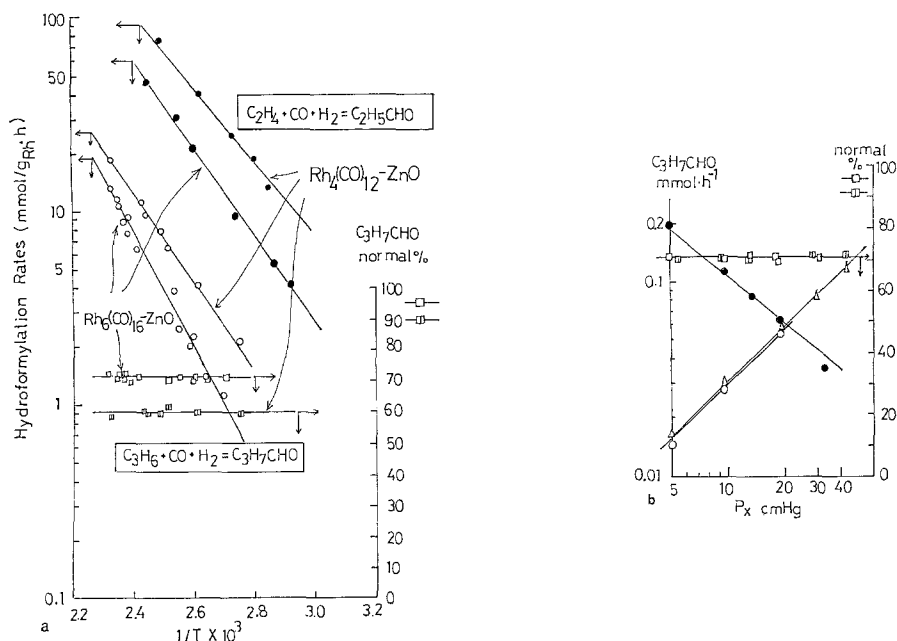


FIG. 3. (a) Temperature dependencies of rates (mmol g<sub>Rh</sub><sup>-1</sup> hr<sup>-1</sup>) and normal-isomer selectivities in ethylene and propene hydroformylations over Rh<sub>4</sub>(CO)<sub>12</sub> and Rh<sub>6</sub>(CO)<sub>16</sub>-derived catalysts. Catalyst preparation: Rh<sub>4</sub>(CO)<sub>12</sub> (0.15 mmol) from hexane solution and Rh<sub>6</sub>(CO)<sub>16</sub> (0.11 mmol) from chloroform solution deposited on ZnO (Kadox 25, 20 g), and with subsequent evacuation in 1 hr at 160°C. Reaction condition: C<sub>2</sub>H<sub>4</sub> (20 cm Hg), CO (20 cm Hg), and H<sub>2</sub> (20 cm Hg); C<sub>3</sub>H<sub>6</sub> (18 cm Hg), CO (18 cm Hg), and H<sub>2</sub> (20 cm Hg). (b) Pressure dependencies of rates (mmol hr<sup>-1</sup>) and normal-isomer selectivity in propene hydroformylation over the catalyst prepared from Rh<sub>6</sub>(CO)<sub>16</sub> (0.09 mmol) on ZnO (20 g) with subsequent evacuation in 1 hr at 160°C. Reaction condition: at 105°C with varying the partial pressures of reactant gases. C<sub>3</sub>H<sub>6</sub>:CO:H<sub>2</sub> = 18:18:P<sub>x</sub> cm Hg (—△—); C<sub>3</sub>H<sub>6</sub>:CO:H<sub>2</sub> = P<sub>y</sub>:18:20 cm Hg (—○—, —□—); C<sub>3</sub>H<sub>6</sub>:CO:H<sub>2</sub> = 18:P<sub>z</sub>:20 cm Hg (—●—, —□—).

carbonyl species similar to partially decarbonylated Rh clusters, which are catalytically active for olefin hydroformylation under mild conditions.

#### *Activities and Selectivities in Propene Hydroformylation Catalyzed by the Cluster-Derived Catalysts from Different Rh Carbonyl Clusters on ZnO*

Rh<sub>4</sub>(CO)<sub>12</sub> and Rh<sub>6</sub>(CO)<sub>16</sub> were deposited into zinc oxide powder (Kadox 25 ZnO) in 0.25 Rh wt% dispersion from hexane and chloroform solutions, respectively. Excess solvent was removed by drying *in vacuo* evaporation at 25°C, and the supported materials were placed in a closed-circulating Pyrex reactor. Re-

moval of CO from each supported carbonyl cluster proceeded almost completely by the heat treatment at 160°C *in vacuo* (ca. 1 hr). When a mixture of C<sub>2</sub>H<sub>4</sub>, CO, and H<sub>2</sub> (molar ratio of 1:1:1, 45–65 cm Hg) was then introduced onto the resulting catalysts, propionaldehyde was catalytically produced at 25 to 140°C with any appreciable induction period. Ethane was slowly formed as a by-product in the reaction. Under stabilized conditions at 25 to 140°C, the C<sub>2</sub>H<sub>6</sub>:C<sub>2</sub>H<sub>5</sub>CHO ratios were 0.1 to 0.5. The apparent activation energies of aldehyde and ethane formations were estimated with 11 and 20 kcal/mole, respectively, over the Rh<sub>4</sub>(CO)<sub>12</sub>-derived catalyst. Propene hy-

TABLE 1

Rates and Isomer Distributions in Ethylene and Propene Hydroformylation Reactions over  $\text{Rh}_4(\text{CO})_{12}$  or  $\text{Rh}_6(\text{CO})_{16}$  Supported on ZnO in Various Degrees of Dispersion after Pretreatment *in Vacuo* or under Hydroformylation Atmosphere

Materials	Pretreatment	$\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$ = $\text{C}_2\text{H}_5\text{CHO}^a$		$\text{C}_3\text{H}_6 + \text{CO} + \text{H}_2$ = $\text{C}_3\text{H}_7\text{CHO}^b$		
		Specific rates (mmole/hr·g <sub>Rh</sub> at 125°C)	AE (kcal/mole)	Specific rates (mmole/g <sub>Rh</sub> hr at 158°C)	Normal %	AE (kcal/mole)
$\text{Rh}_4(\text{CO})_{12}\text{-ZnO}^c$ (0.15 mmole-20 g)	{Evacuation <sup>d</sup> Activation <sup>e</sup> under hydroformylation atm	96	11	18	58	13.5
		86	12	16	60	14
$\text{Rh}_6(\text{CO})_{16}\text{-ZnO}$ (0.11 mmole-20 g)	{Evacuation Activation under hydroformylation atm	35	13	13	70	15
		30	14	9	72	16
$\text{Rh}_6(\text{CO})_{16}\text{-ZnO}$ (0.03 mmole-20 g)	Evacuation	30	13	10	72	15
$\text{Rh}_6(\text{CO})_{16}\text{-ZnO}$ (0.19 mmole-20 g)	Evacuation	25	13	6	70	16

<sup>a</sup>  $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 20:20:20$  cm Hg.

<sup>b</sup>  $\text{C}_3\text{H}_6:\text{CO}:\text{H}_2 = 18:20:20$  cm Hg.

<sup>c</sup> Kadox 25-ZnO, preheating at 350°C for 15 hr prior to use.

<sup>d</sup> Evacuation of the supported materials at 160°C in 1 hr ( $10^{-4}$  Torr).

<sup>e</sup> Rates and isomer selectivities were observed after the steady-state of the hydroformylation reactions was realized under atmosphere of  $\text{C}_2\text{H}_4$  (or  $\text{C}_3\text{H}_6$ ), CO, and  $\text{H}_2$  at 110 to 150°C.

droformylation reaction also took place to produce a mixture of normal and iso- $\text{C}_3\text{H}_7\text{CHO}$ . The linear isomer selectivity in propene hydroformylation with the catalyst covered 56 to 60 normal% over the wide range of temperature applied, as shown in Fig. 3a. On the other hand, the  $\text{Rh}_6(\text{CO})_{16}$ -derived catalyst gave higher proportions of linear aldehyde at levels of 68 to 72 normal% selectivity, independent of reaction temperature (90–160°C). The linear isomer selectivity was also nearly independent of CO and  $\text{H}_2$  partial pressure (5–45 cm Hg), as indicated in Fig. 3b. The results presented in Table 1 show that hydroformylation rates and linear isomer proportions obtained with

pyrolyzed cluster catalysts are relatively structure sensitive to the precursor carbonyl clusters. The catalyst prepared from  $\text{Rh}_4(\text{CO})_{12}$  exhibited specific rates of aldehyde formation 1.5 to 2.8 times larger than that from  $\text{Rh}_6(\text{CO})_{16}$ ; however, the former showed a lower proportion of linear isomer. The specific rates and isomer selectivities were consistently obtained over those cluster-derived catalysts under the different catalyst preparations (pyrolysis of the supported materials *in vacuo*, under hydroformylation and hydrogen atmosphere) and with varying the degrees of Rh dispersion on ZnO. Accordingly, the results suggest that the catalytic behaviors of the cluster-derived catalysts in

olefin hydroformylation were relatively characteristic of the sorts of precursor Rh carbonyl clusters employed.

Other Rh carbonyl clusters such as  $\text{Rh}_7(\text{CO})_{16}3\text{NEt}_4$  (in acetone) and  $\text{Rh}_{13}(\text{CO})_{23}\text{H}_{2-3}2\text{NBu}_4$  (in THF) were also used to prepare the cluster-derived catalysts. Removal of CO and organic residues was similarly accomplished by evacuating the supported materials (ca. 0.25 Rh wt% loading) at 160 to 180°C. The rates and linear isomer selectivities in propene hydroformylation were summarized in Table 2 with the catalysts prepared from various kinds of carbonyl clusters. The specific activity order at 158°C for precursor Rh carbonyl clusters supported on ZnO was:  $\text{Rh}_4(\text{CO})_{12} > \text{Rh}_6(\text{CO})_{16} > \text{Rh}_7(\text{CO})_{16}3\text{NEt}_4 > \text{Rh}_{13}(\text{CO})_{23}\text{H}_{2-3}2\text{NBu}_4$  with a total range of  $\sim 10$ . In contrast, normal isomer selectivities relatively increased over the catalysts from larger Rh carbonyl clusters. For comparison, the Rh supported metal catalysts were conventionally prepared from Rh complexes  $\text{Rh}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  and  $\text{Rh}_2(\text{CO})_3(\pi\text{-C}_5\text{H}_5)_2$  and Rh salts ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ) impregnated on ZnO,

silica, and  $\gamma\text{-Al}_2\text{O}_3$ , which were followed with subsequent hydrogen reduction (1 atm, 350°C for 15 hr). They showed negligible or lower conversions of ethylene and propene hydroformylations under similar reaction conditions, and the hydrogenation to paraffin dominantly occurred. When  $\text{RhCl}_3$ ,  $\text{Rh}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ , and  $\text{Rh}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)$  were simply deposited from their solutions onto ZnO (Kadox 25) and silica gel (AEROSIL-300) in 0.5 to 1.5 Rh wt% loading, propionaldehyde was produced with minute conversions (less than 5 mole% in 20 hr) in the initial stage of ethylene hydroformylation at 100°C. The hydroformylation activities of those supported mono-Rh complex catalysts rapidly decreased, and completely lost in the prolonged reaction. A considerable amount of starting Rh complexes or  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  (formed on silica between  $\text{RhCl}_3$  and CO under the reaction condition) was eliminated onto the wall of the glass reactor. Accordingly, the results may suggest that Rh carbonyl clusters such as  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  would be effective precursors to prepare the catalytically active

TABLE 2  
Specific Rates and Normal-Isomer Selectivities in Propene Hydroformylation over Various Rh Carbonyl Clusters Supported on ZnO

Precursor Rh compound	Rh wt <sup>a</sup> loading (mg)	Specific rate <sup>b</sup> (mmol/g <sub>Rh</sub> hr at 158°C)	Normal-isomer <sup>c</sup> selectivity (mole%)	AE (kcal/mol)
$\text{Rh}_4(\text{CO})_{12}$	55	20	58 ± 2	14
$\text{Rh}_6(\text{CO})_{16}$	58	12	70 ± 2	15.5
$\text{Rh}_7(\text{CO})_{16}3\text{NEt}_4$	52	4.1	72 ± 2	16
$\text{Rh}_{13}(\text{CO})_{23}\text{H}_{2-3}2\text{NBu}_4$	38	2.2	72 ± 2	16.5
$\text{Rh}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$	85	0.23	52 ± 2	
$\text{Rh}_2(\text{CO})_3(\pi\text{-C}_5\text{H}_5)_2$	50	6.8	61 ± 2	14
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ reduced $\text{H}_2$ (1 atm, 350°C)	250	Less than 0.01		

<sup>a</sup> Each rhodium compound was supported on ZnO (20 g). The supported materials were evacuated at 160°C, 2 hr, and followed with the subsequent hydrogen treatment.

<sup>b</sup>  $\text{C}_3\text{H}_6:\text{CO}:\text{H}_2 = 18:18:20$  cm Hg. The reaction was carried out in the circulating closed reactor (ca. 420 ml).

<sup>c</sup>  $n\text{-C}_3\text{H}_7\text{CHO}/n\text{-C}_3\text{H}_7\text{CHO} + \text{iso-C}_3\text{H}_7\text{CHO} \times 100$  (mol%).

TABLE 3  
Specific Rates and *n*-Isomer Selectivities in Propene Hydroformylation over  $\text{Rh}_4(\text{CO})_{12}$   
and  $\text{Rh}_6(\text{CO})_{16}$  Supported on Various Metal Oxides

Materials	Pretreatment	Specific rate <sup>a</sup> of hydroformylation (mmole/hr·g <sub>Rh</sub> , 155°C)	$\text{C}_3\text{H}_7\text{CHO}$ <i>n</i> -isomer (%) <sup>b</sup>	$\text{C}_3\text{H}_7\text{CHO}(\text{C}_3\text{H}_7\text{CHO}$ + $\text{C}_4\text{H}_9\text{OH})$ × 100 (mole%)
$\text{Rh}_6(\text{CO})_{16}\text{-MgO}$ (0.10 mmole-20 g)	{Evacuation <sup>c</sup>	7	32	78
	{Activation under <sup>d</sup> hydroformylation atmosphere	3	45	85
$\text{Rh}_4(\text{CO})_{12}\text{-TiO}_2$ (0.15 mmole-20 g)	Evacuation	4	56	70
$\text{Rh}_6(\text{CO})_{16}\text{-TiO}_2$ (0.11 mmole-20 g)	Evacuation	1.5	62	86
$\text{Rh}_4(\text{CO})_{12}\text{-La}_2\text{O}_3$ (0.15 mmole-20 g)	Evacuation	7.5	68	45
$\text{Rh}_6(\text{CO})_{16}\text{-La}_2\text{O}_3$ (0.12 mmole-20 g)	Evacuation	3	75	50
$\text{Rh}_4(\text{CO})_{12}\text{-SiO}_2$ (0.15 mmole-5 g)	Evacuation	0.4	63	75
$\text{Rh}_4(\text{CO})_{12}\text{-Al}_2\text{O}_3$ (0.11 mmole-20 g)	{Evacuation	Less than 0.01	50	25
	{Activation under hydroformylation atmosphere	Less than 0.01	53	30

<sup>a</sup>  $\text{C}_3\text{H}_6:\text{CO}:\text{H}_2 = 18:18:20$  cm Hg.

<sup>b</sup>  $n\text{-C}_3\text{H}_7\text{CHO}/n\text{-C}_3\text{H}_7\text{CHO} + \text{iso-C}_3\text{H}_7\text{CHO} \times 100$  mole%.

<sup>c</sup> Evacuation of the resulting material at 160°C,  $10^{-4}$  Torr.

<sup>d</sup> Rates and *n*-isomer selectivities were measured after the stationary state of hydroformylation was realized at 130 to 160°C.

supported catalysts for vapor-phase hydroformylations under the mild reaction conditions.

#### *Effects of Metal Oxides Supporting Rh Carbonyl Clusters*

Other basic oxides such as MgO,  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  were found to act as alternative carriers in preparation of the Rh cluster-derived catalysts active for olefin hydroformylation.  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  were deposited similarly from the solutions onto magnesium oxide (MgO from Merck Chem. Reagent Co., 99.9% 35 m<sup>2</sup>/g), lanthanum oxide ( $\text{La}_2\text{O}_3$  from

Nakarai Chem. Co., 99.9% 25 m<sup>2</sup>/g), titanium oxide ( $\text{TiO}_2$  from Merck Co., 99.9% 40 m<sup>2</sup>/g), and zirconium oxide ( $\text{ZrO}_2$  from Nakarai Chem. Co., 99.9% 23 m<sup>2</sup>/g). Those metal oxides were evacuated at 320°C for 15 hr, prior to use. Each supported material was subjected by heat treatment at 160°C or under hydroformylation atmosphere at 100 to 150°C. The rates and isomer distributions in ethylene and/or propene hydroformylation reactions were studied at various temperatures (90–160°C) and pressures [ $\text{C}_2\text{H}_4$  (or  $\text{C}_3\text{H}_6$ ): $\text{CO}:\text{H}_2 = 1:1\text{--}2:1\text{--}2$ , total pressure of 45–60 cm Hg]. The typical results



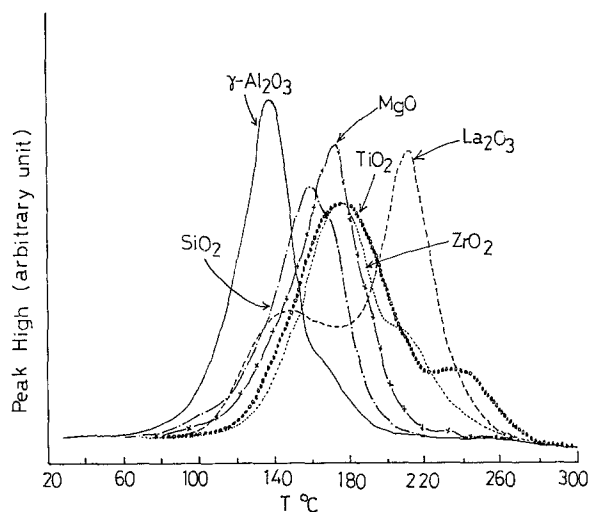


FIG. 4. Patterns of temperature-programmed CO evolution of  $\text{Rh}_6(\text{CO})_{16}$  dispersed on various metal oxides. Materials:  $\text{Rh}_6(\text{CO})_{16}$  deposited on MgO (0.5 Rh wt%) ( $-\times-\times-$ ), on  $\text{La}_2\text{O}_3$  (0.5 Rh wt%) ( $-\cdot-\cdot-$ ), on  $\text{TiO}_2$  (0.5 Rh wt%) ( $\circ\circ\circ\circ\circ\circ\circ\circ$ ), on  $\text{ZrO}_2$  (0.25 Rh wt%) ( $-\cdot-\cdot-$ ), on silica gel (1.0 Rh wt%) ( $-\cdot-\cdot-$ ), and on  $\gamma\text{-Al}_2\text{O}_3$  (1.7 Rh wt%) ( $-\cdot-\cdot-$ ), respectively. Experimental conditions: He 1 atm, 100 ml/min flow,  $5^\circ\text{C}/\text{min}$  (programmed temperature raising), detected with TCD gas chromatography using AC 1 m column at  $25^\circ\text{C}$ .

were summarized in Table 3. It was found that further hydrogenation to alcohol simultaneously proceeded in the reaction over the catalysts with those oxides, and, rather surprisingly, that the isomer selectivity in propene hydroformylation depended relatively on the sorts of oxides. In particular, iso-aldehyde was preferentially produced when  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  were supported on MgO,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ . The series of metal oxides are characterized by Tanabe (16) as basic oxides having a small amount of weak surface acidity. In contrast to the basic oxide carriers, hydroformylation reaction first occurred after the prolonged induction period (20–40 hr) over the catalyst of  $\text{Rh}_4(\text{CO})_{12}$  or  $\text{Rh}_6(\text{CO})_{16}$  supported on silica gel. The hydroformylation activities were considerably enhanced with subsequent hydrogen reduction [ $\text{H}_2$  (1 atm) at  $200^\circ\text{C}$  for 5 hr]. On the other hand, some typical acidic oxides such as  $\gamma\text{-Al}_2\text{O}_3$  (A-11 Harshaw Co.,  $280\text{ m}^2/\text{g}$  S.A.), Zeolite 13X (Merck Co.,  $250\text{ m}^2/\text{g}$ ),  $\text{V}_2\text{O}_5$  (Wako Pure Chem. Co., 99.9%), and

$\text{P}_2\text{O}_5$  (Wako Pure Chem. Co., 99.9%) powders were employed to prepare the cluster-supported catalysts. The resulting catalysts exhibited negligible hydroformylation activities under the similar reaction conditions. A trace of aldehyde and alcohol were produced only in the prolonged reaction at elevated temperatures (above  $150^\circ\text{C}$ ), and even with the subsequent hydrogen reduction.

The states of metal-carbonyl bonding in the supported clusters may be informed from the results with the TPD patterns of  $\text{Rh}_6(\text{CO})_{16}$  dispersed on each metal oxide. As presented in Fig. 4, it was suggested that evolution of CO occurred at temperatures lower than  $155$  to  $160^\circ\text{C}$  [the decomposition temperature of  $\text{Rh}_6(\text{CO})_{16}$  in solid (11)], when it was supported on acidic oxides such as  $\gamma\text{-Al}_2\text{O}_3$  and silica gel. On the other hand, removal of CO was observed at the temperatures relatively higher than  $160^\circ\text{C}$  when  $\text{Rh}_6(\text{CO})_{16}$  was dispersed on basic oxides such as ZnO, MgO,  $\text{La}_2\text{O}_3$ , and  $\text{ZrO}_2$ . The results may suggest that Rh carbonyl

TABLE 4

The Specific Rates and Normal-Isomer Selectivities in Propene Hydroformylation over ZnO-Supported  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ ,  $\text{RhCo}_3(\text{CO})_{12}$ , and  $\text{Co}_4(\text{CO})_{12}$

Catalyst <sup>a</sup>	Specific rates of <sup>b</sup> aldehyde formation (mmol/g <sub>M</sub> hr at 160°C)	Normal-isomer <sup>c</sup> selectivity (mole%)	Apparent AE (kcal/mol)
$\text{Rh}_4(\text{CO})_{12}\text{-ZnO}$	21	58 ± 2	10.5
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}\text{-ZnO}$	13	70 ± 3	12.8
$\text{RhCo}_3(\text{CO})_{12}\text{-ZnO}$	9	80 ± 1	13.3
$\text{Co}_4(\text{CO})_{12}\text{-ZnO}$	1.2	90 ± 2	17.9
(1 $\text{Rh}_4(\text{CO})_{12}$ + 1 $\text{Co}_4(\text{CO})_{12}$ )-ZnO (0.075 mmole) (0.080 mmole)	11	62 ± 3	13.6
(1 $\text{Rh}_4(\text{CO})_{12}$ + 3 $\text{Co}_4(\text{CO})_{12}$ )-ZnO (0.040 mmole) (0.12 mmole)	6	65 ± 2	14.5

<sup>a</sup> Carbonyl clusters (0.15 mmol) were deposited on ZnO (20 g) from hexane solutions. Pyrolysis at 160°C under evacuation.

<sup>b</sup> Reaction conditions:  $\text{C}_3\text{H}_6:\text{CO}:\text{H}_2 = 18:18:20$  cm Hg. The average circulation rates of gas were ca. 80 ml/min. The total volume of the Pyrex glass reactor was 420 ml.

<sup>c</sup>  $n\text{-C}_3\text{H}_7\text{CHO}/n\text{-C}_3\text{H}_7\text{CHO} + \text{iso-C}_3\text{H}_7\text{CHO} \times 100$  (mole%). The normal-isomer selectivities observed on each supported catalyst were almost constant over the wide range of the reaction temperature.

clusters would be stabilized, and metal-carbonyl bonding be strengthened in dispersion on basic oxides.

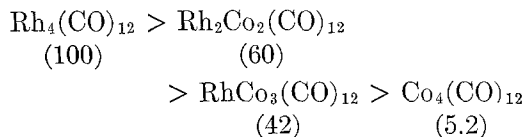
It was also found that, in contrast to the catalyst supported on ZnO, the ir carbonyl bands of  $\text{Rh}_6(\text{CO})_{16}$  changed irreversibly by supporting it on  $\gamma\text{-Al}_2\text{O}_3$  or silica gel. The characteristic CO bands of the supported material appeared in the region of 2020, 2075  $\text{cm}^{-1}$  (twin), and 1800  $\text{cm}^{-1}$  (bridging), similarly reported by Smith *et al.* (17). By subjecting to heat treatment at 90 to 150°C under a mixture of ethylene, CO, and  $\text{H}_2$  (total pressure of 45 cm Hg), the original carbonyl bands of supported  $\text{Rh}_6(\text{CO})_{16}$  decreased, and irreversibly shifted to higher wave numbers of 2050, 2090, and 1860  $\text{cm}^{-1}$ , respectively. The similar carbonyl ir spectrum was also observed in CO chemisorption over the supported Rh metal (8), which was prepared from  $\text{RhCl}_3$  impregnated on  $\gamma\text{-Al}_2\text{O}_3$  with subsequent hydrogen reduction. This may suggest that the Rh clusters dispersed on acidic carriers such as alumina

and silica hardly hold their unique cluster-carbonyls, and lose the lower-valent metal state, probably due to a strong interaction with acidic surface of the oxides. The supported materials on acidic oxides were catalytically inactive for olefin hydroformylation.

#### *The Catalysts Prepared from Bimetallic Rh-Co and Co Carbonyl Clusters Supported on ZnO*

Ethylene and propene hydroformylation reactions also proceeded over the bimetallic Rh-Co and Co carbonyl clusters supported on ZnO.  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ ,  $\text{RhCo}_3(\text{CO})_{12}$ , and  $\text{Co}_4(\text{CO})_{12}$  were similarly deposited onto ZnO powder from hexane solutions in 0.25 metal wt% dispersion. The supported materials were subsequently evacuated at 160°C in 1 hr, and the hydroformylation gas was admitted onto the resulting catalysts. The typical results were presented in Table 4. The specific activity order in propene hydroformylation for the sup-

ported clusters was:



where the figures in parentheses are relative rates of aldehyde formation at 160°C. For the bimetallic Rh-Co cluster-derived catalysts, the specific hydroformylation activities in Rh weight basis were almost comparable to the  $\text{Rh}_4(\text{CO})_{12}$  derived catalyst under the similar reaction conditions. This suggests that each rhodium atom in Rh and bimetallic Rh-Co clusters supported on ZnO may act almost equally for the hydroformylation reactions. On the other hand, catalysts from clusters having larger cobalt contents produced higher proportions of linear aldehyde. The normal isomer selectivity observed on each supported catalyst was almost independent upon the reaction temperatures (50–200°C) and as well as upon varying the partial pressure of CO and  $\text{H}_2$ . Although the  $\text{Co}_4(\text{CO})_{12}$  derived catalyst gave above 90% normal-isomer selectivity in propene hydroformylation, its specific rates were considerably lower (more than 15 times smaller in metal weight basis) than those over the  $\text{Rh}_4(\text{CO})_{12}$ -derived catalyst. Accordingly, such higher normal-isomer selectivities of the mixed Rh-Co cluster catalysts could not be explained simply by the additional aldehyde formation catalyzed with individual Rh and Co cluster-derived catalysts. In fact, when a mixture of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  (1:1 and 1:3 molar ratios) was deposited onto ZnO powder from the mixture solutions, the mixed catalysts derived from individual Rh and Co clusters were prepared in similar preparation procedures. The normal-isomer selectivities in propene hydroformylation catalyzed by the resulting materials were comparatively lower than those by the catalysts derived from the

bimetallic Rh-Co carbonyl clusters, as illustrated in Table 4. This may suggest that each supported Rh and Co carbonyl clusters in the mixed system catalyzed independently the propene hydroformylation reaction. The supported bimetallic Rh-Co clusters on ZnO might behave as "highly dispersed alloys" having compositions similar to those of the corresponding precursor carbonyl clusters, as Anderson *et al.* have previously suggested on the system of alumina-supported bimetallic Rh-Co clusters (3). Furthermore, it may suggest that cobalt atoms in supported bimetallic Rh-Co clusters play a part as an "electronic donor-ligand" to enhance the normal-isomer formation, possibly due to their lower ionization potential than rhodium. A normal carbanion-intermediate might be stabilized (18) on top of electron-rich Rh site, which is active for olefin hydroformylation reaction under mild reaction conditions.

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