

An Infrared Study of the Rh-Y Zeolite Related to Activity for Ethylene Hydroformylation

NOBUO TAKAHASHI,¹ AKIHIKO MIJIN, HANZO SUEMATSU, SHURI SHINOHARA, AND HIDEKI MATSUOKA

Department of Industrial Chemistry, Kitami Institute of Technology, 165 Koencho, Kitami, Hokkaido 090, Japan

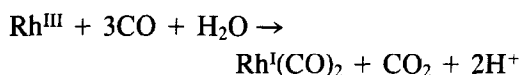
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Two types of CO-Rh species formed on the Rh-Y zeolite, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Rh}^{\text{I}}(\text{CO})_2$, were exposed to various atmospheres containing reaction components of ethylene hydroformylation. During exposure of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ to $\text{C}_2\text{H}_4 + \text{H}_2$, $\text{Rh}_6(\text{CO})_{16}$ was decomposed and some CO molecules were converted into propionaldehyde. In the case of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$, only a very small decrease in IR bands due to $\text{Rh}^{\text{I}}(\text{CO})_2$ was observed, while the formation of propionaldehyde was not appreciable. The sample once exposed to $\text{C}_2\text{H}_4 + \text{H}_2$, however, became active for ethylene hydroformylation. During exposure of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ to a reaction mixture for ethylene hydroformylation, neither changes in the IR bands due to $\text{Rh}_6(\text{CO})_{16}$ modification nor formation of propionaldehyde was observed. In the case of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$, almost no changes were observed in the bands due to $\text{Rh}^{\text{I}}(\text{CO})_2$. However, a small amount of propionaldehyde was formed during the exposure, while the formation was not important compared with that on the $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ once exposed to $\text{C}_2\text{H}_4 + \text{H}_2$. The change in color of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ from light yellow to gray was observed during the exposure to $\text{C}_2\text{H}_4 + \text{H}_2$ or $\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$. The catalytic activity of Rh-Y for ethylene hydroformylation was considerably enhanced by pretreatment of the fresh Rh-Y with H_2 . The predominant rhodium species on the sample exposed to H_2 at 393 K were found to be metallic rhodium by X-ray photoelectron spectroscopy. © 1989 Academic Press, Inc.

INTRODUCTION

The Rh-Y zeolite has been known to be active for olefin hydroformylation (1-7). It has been clarified that the following two CO-Rh species are possibly formed under hydroformylation conditions at atmospheric pressure. The first type of CO-Rh species is characterized by IR bands at 2098 and 1763 cm^{-1} . This species was first observed by Mantovani *et al.* (1) on the Rh-Y pretreated with a gas mixture of CO:H₂ (1:1, 8 MPa) at 403 K, and it has been attributed to $\text{Rh}_6(\text{CO})_{16}$ species formed on zeolites (7-11). The second type of CO-Rh species is characterized by IR bands at 2115, 2098, 2044, and 2019 cm^{-1} . The four bands observed have been decomposed into two doublets attributed to two kinds of geminal dicarbonyl rhodium species, Rh^{I}

$(\text{CO})_2$, which are formed by the reaction (12-14)



Doublets at 2098-2019 and 2115-2044 cm^{-1} are attributed to $\text{Rh}^{\text{I}}(\text{CO})_2(\text{O}_z)_2$ and $\text{Rh}^{\text{I}}(\text{CO})_2(\text{O}_z)(\text{H}_2\text{O})$, respectively, by Shannon *et al.*, where O_z represents a zeolite framework oxygen atom (14). The type of CO-Rh species formed by a reaction of Rh^{III} with CO on the Rh-Y zeolite strongly depends on the water content of the sample (7, 9, 11, 15). The first type of CO-Rh species, $\text{Rh}_6(\text{CO})_{16}$, is favorably formed on the Rh-Y zeolite with relatively high water content, while the second one, $\text{Rh}^{\text{I}}(\text{CO})_2$, is predominantly formed on the Rh-Y zeolite with relatively low water content. Thus, the Rh-Y zeolite which predominantly contains each one of the CO-Rh species can be prepared. Davis *et al.* (5-7) compared cata-

¹ To whom correspondence should be addressed.

lytic behaviors of Rh-X and Rh-Y zeolites for propylene hydroformylation, where predominant formation of $\text{Rh}_6(\text{CO})_{16}$ species on the Rh-Y zeolite or $\text{Rh}^1(\text{CO})_2$ species on the Rh-X zeolite was observed. Although different in the kind of CO-Rh species incorporated, both Rh zeolites could catalyze propylene hydroformylation with almost the same apparent activation energy. However, further details of active rhodium species have not been reported.

EXPERIMENTAL

The Rh-Y zeolite containing 65×10^{-6} mol Rh (g cat) $^{-1}$ was prepared from the Na-Y zeolite (obtained from Toyo Soda Manufacturing Co., Ltd., as a fine powder without binder) and an aqueous solution of rhodium trichloride trihydrate by stirring the mixture at 353 K for 12 h. After the solid was thoroughly washed with distilled water, it was dried at 393 K overnight. For IR experiments, about 100 mg of Rh-Y zeolite was pressed into a thin circular disk. The sample was placed in a glass IR cell equipped with KBr windows (distance between the windows was 5 mm), which was connectable to a conventional vacuum line (a volume of the system is 380 cm³). Evacuation of the sample at desired temperatures was followed by exposure to CO at 393 K for 3 h (the amount of CO introduced was 4.8×10^{-4} mol, which corresponds to a pressure of 3.0 kPa at 293 K). After the sample was cooled below 323 K, it was evacuated for 5 min prior to an IR measurement. Subsequent exposure of the sample to various atmospheres was carried out in the same apparatus. Usually, the amount of each component introduced into the system was the same as the amount of CO for adsorption unless otherwise noted; e.g., a total pressure of $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2$ (1:1:1) was 9.0 kPa at 293 K. IR measurements were carried out at room temperature by using a transmission method with a Fourier-transform IR spectrometer (JEOL, Ltd., JIR-40X) with a resolution of 4 cm $^{-1}$. Measurements for X-ray photoelectron

spectroscopy were carried out using a Rigaku XPS-7000 photoelectron spectrometer employing AlK α X-radiation with the cooperation of Rigaku Industrial Co.

RESULTS AND DISCUSSION

A typical IR spectrum of CO, adsorbed on the Rh-Y zeolite with relatively high water content (evacuated at 293 K for 5 min) at 393 K for 3 h, is shown by spectrum (a) in Fig. 1. The CO-Rh species formed are characterized by two IR bands at 2098 and 1760 cm $^{-1}$, indicating that $\text{Rh}_6(\text{CO})_{16}$ species are mainly formed on this sample.

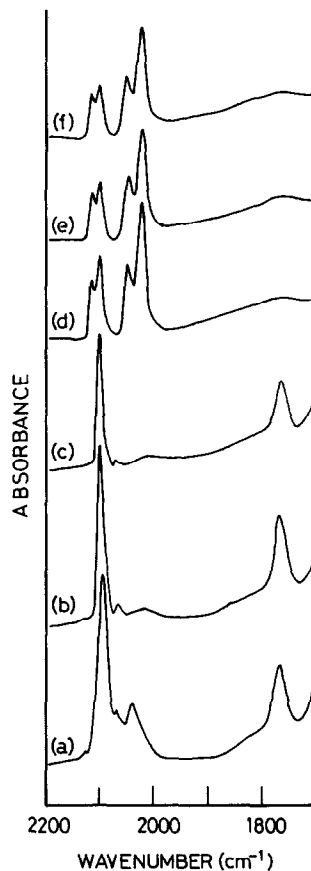


FIG. 1. Reaction of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ and $\text{Rh}^1(\text{CO})_2/\text{Y}$ with hydrogen. (a) $\text{Rh}_6(\text{CO})_{16}/\text{Y}$; (b) after exposure of sample (a) to H_2 at 423 K for 2 h; (c) sample (b) exposed to H_2 at 423 K for 5 h; (d) $\text{Rh}^1(\text{CO})_2/\text{Y}$; (e) after exposure of sample (d) to H_2 at 423 K for 3 h; (f) sample (e) exposed to H_2 at 423 K for 5 h.

This sample is denoted by $\text{Rh}_6(\text{CO})_{16}/\text{Y}$. However, the CO–Rh species formed on the Rh–Y zeolite with relatively low water content (evacuated at 393 K for 3 h) are characterized by four sharp bands at 2115, 2098, 2044, and 2019 cm^{-1} as shown by spectrum (d) in Fig. 1, suggesting predominant formation of two kinds of geminal dicarbonyl species of monovalent rhodium on this sample. This sample is denoted by $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$.

The sample of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ was exposed to H_2 at 423 K. As shown by spectrum (b) in Fig. 1, almost no appreciable changes were observed with respect to the bands at 2098 and 1760 cm^{-1} after 2 h of the exposure, while the band around 2040 cm^{-1} disappeared and the band at 2098 cm^{-1} was narrowed. Further exposure of the sample to H_2 at 423 K slightly reduced the intensities of the two bands due to $\text{Rh}_6(\text{CO})_{16}$ as shown by spectrum (c). On the sample of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$, the intensities of four bands decreased very slowly during exposure to H_2 at 423 K as shown by spectra (e) and (f) in Fig. 1. These results indicate that both types of CO–Rh species can react with H_2 , while the rates are slow at 423 K.

Effects of C_2H_4 on $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ are shown in Fig. 2. Admitting C_2H_4 into the system increases intensities of the bands at 2115 and 2044 cm^{-1} and decreases those of the bands at 2098 and 2019 cm^{-1} as shown by spectrum (b) (this spectrum was recorded without evacuation of the sample). Also, new bands around 1450 cm^{-1} appeared. The new bands are attributed to the ethylene adsorbed, since a sample of the Na–Y zeolite with adsorption of C_2H_4 showed the corresponding bands as shown by spectrum (h). After evacuation of sample (b) at 393 K for 10 min, the bands due to C_2H_4 disappeared and the reversion in intensities was observed on the four bands as shown by spectrum (c). These results indicate that the majority of CO molecules in $\text{Rh}^{\text{I}}(\text{CO})_2$ would not be consumed during the exposure to C_2H_4 . The CO–Rh species characterized by IR bands at 2110 and 2044 cm^{-1} has been

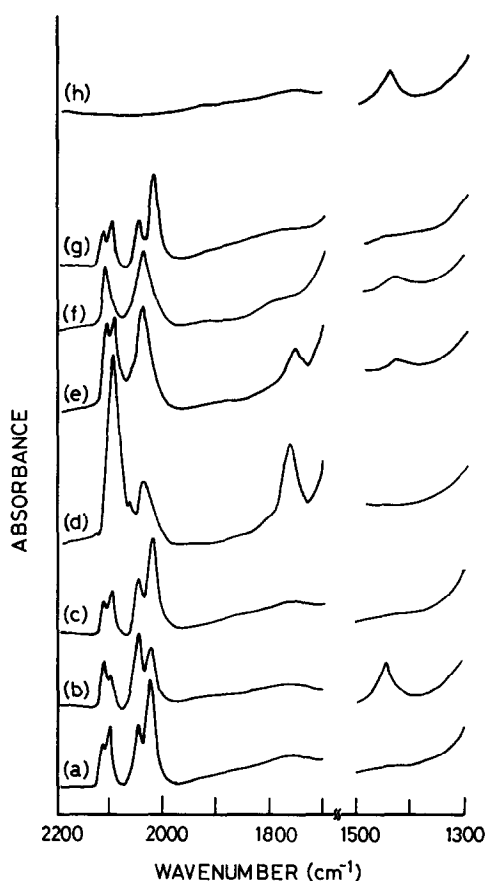


FIG. 2. Reaction of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ and $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ with ethylene. (a) $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$; (b) after exposure of sample (a) to C_2H_4 (7.9×10^{-4} mol) at 393 K for 1 h; (c) after evacuation of sample (b) at 393 K for 15 min; (d) $\text{Rh}_6(\text{CO})_{16}/\text{Y}$; (e) after exposure of sample (d) to C_2H_4 at 393 K for 2 h; (f) sample (e) exposed to C_2H_4 at 393 K for 8 h; (g) sample (f) followed by evacuation at 393 K for 10 min; (h) Na–Y exposed to C_2H_4 at 393 K for 1 h. Spectra (b), (e), (f), and (h) were recorded in the presence of C_2H_4 in gas phase.

attributed to $\text{Rh}^{\text{I}}(\text{CO})_2(\text{C}_2\text{H}_4)$ species by Lefebvre and Ben Taarit (16). On the other hand, $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ was considerably influenced by C_2H_4 . Namely, intensities of the bands at 2098 and 1760 cm^{-1} decreased with time on exposure to C_2H_4 . After the exposure for 10 h, the bands at 2110 and 2040 cm^{-1} are found to be predominant as shown by spectrum (f). Spectra (e) and (f) were recorded in the presence of C_2H_4 in the gas phase. After evacuation of sample (f) at 393

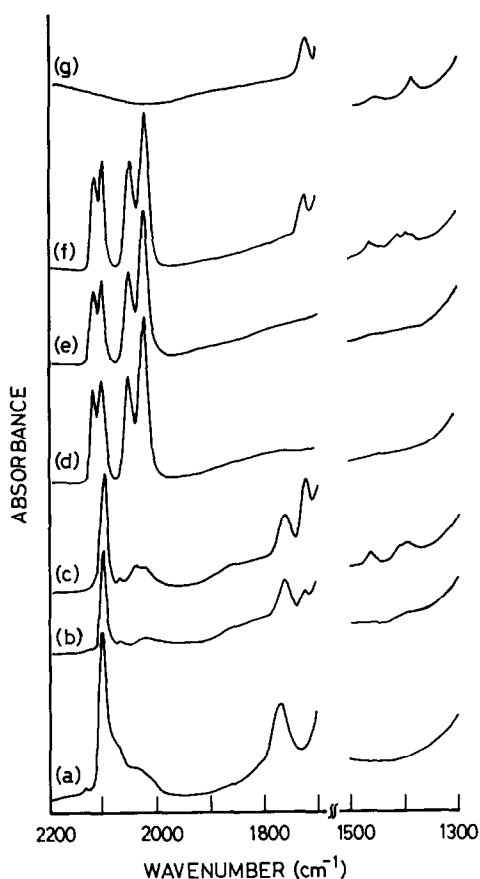


FIG. 3. Reaction of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ and $\text{Rh}^1(\text{CO})_2/\text{Y}$ with $\text{C}_2\text{H}_4 + \text{H}_2$. (a) $\text{Rh}_6(\text{CO})_{16}/\text{Y}$; (b) after exposure of sample (a) to $\text{C}_2\text{H}_4:\text{H}_2$ (1:1) at 393 K for 4 h; (c) sample (b) followed by exposure to $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2$ (1:1:1) at 393 K for 5 h; (d) $\text{Rh}^1(\text{CO})_2/\text{Y}$; (e) after exposure of sample (d) to $\text{C}_2\text{H}_4:\text{H}_2$ (1:1) at 393 K for 3 h (the spectrum was recorded in the presence of the gas mixture in gas phase); (f) sample (e) followed by exposure to $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2$ (1:1:1) at 393 K for 4 h; (g) Na-Y exposed to propionaldehyde at 393 K for 1 h.

K for 10 min, spectrum (g) was obtained, suggesting conversion of some $\text{Rh}_6(\text{CO})_{16}$ into $\text{Rh}^1(\text{CO})_2$ during exposure to C_2H_4 . However, this conversion was suppressed in the presence of CO in the gas phase. Essentially the same effects of propylene as of ethylene on both types of CO-Rh species were observed. The CO-Rh species observed in the presence of C_3H_6 (2110 and 2040 cm^{-1}) has been attributed to $\text{Rh}^1(\text{CO})_2$ (C_3H_6) species by Rode *et al.* (7). However,

a considerable decrease in C_3H_6 pressure was observed during exposure of the samples to C_3H_6 at 393 K. It has been reported that oligomerization of C_3H_6 is catalyzed by acid sites on the Rh-Y zeolite, and the reaction becomes important at temperatures higher than 373 K (17).

In order to clarify whether CO molecules themselves in the CO-Rh species can react with C_2H_4 and H_2 to form propionaldehyde, the two types of samples were exposed to a mixture of $\text{C}_2\text{H}_4 + \text{H}_2$. The spectrum (g) in Fig. 3 was obtained on a sample of Na-Y zeolite with adsorption of propionaldehyde. If hydroformylation took place during the exposure, a band at 1720 cm^{-1} ($-\text{CHO}$) and several bands around 1400–1500 cm^{-1} should be observed in a spectrum, since the propionaldehyde formed was strongly adsorbed on the catalyst (3, 4). As shown by spectrum (b) in Fig. 3, the intensities of the bands at 2098 and 1763 cm^{-1} on $\text{Rh}_6(\text{CO})_{16}$ decreased after exposure of the sample to the mixture. In this case, the bands at 1720 and 1400–1500 cm^{-1} appeared, suggesting the transformation of some CO molecules on $\text{Rh}_6(\text{CO})_{16}$ into propionaldehyde during exposure to $\text{C}_2\text{H}_4 + \text{H}_2$. As shown by spectrum (e) in Fig. 3, however, almost no appreciable changes were observed on the four bands due to $\text{Rh}^1(\text{CO})_2$ during exposure of $\text{Rh}^1(\text{CO})_2/\text{Y}$ to the mixture of $\text{C}_2\text{H}_4 + \text{H}_2$ at 393 K. No bands due to propionaldehyde were observed. In this case, a color of the sample turned from light yellow to gray, and a considerable decrease in pressure of the reaction mixture due to hydrogenation of ethylene was observed. The reason why no appreciable bands due to C_2H_4 were observed in spectrum (e) would be fast consumption of C_2H_4 by hydrogenation. In such a case, the majority of $\text{Rh}^1(\text{CO})_2$ could not be exposed to $\text{C}_2\text{H}_4 + \text{H}_2$. Namely, it is impossible to evaluate a reactivity of CO in $\text{Rh}^1(\text{CO})_2$ with $\text{C}_2\text{H}_4 + \text{H}_2$ from the results shown in Fig. 3.

The sample of $\text{Rh}_6(\text{CO})_{16}$ was exposed to a mixture of $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2$ (1:1:1) at 393 K, in order to clarify its ability for ethylene

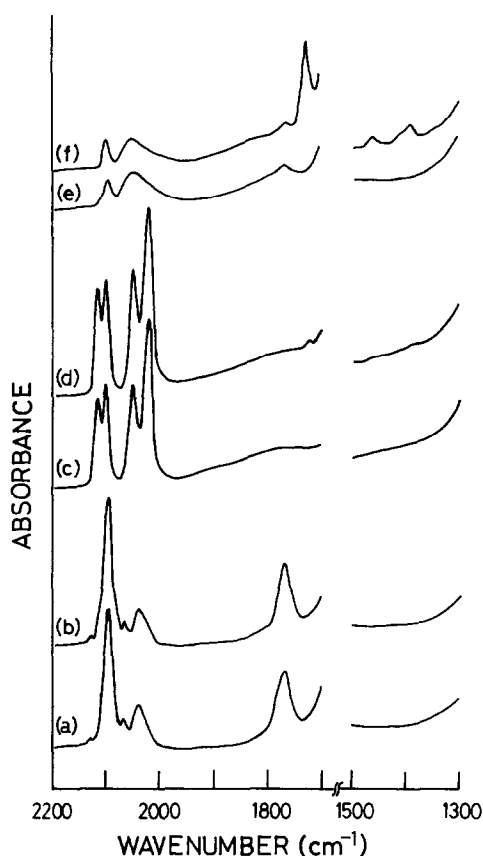


FIG. 4. Reaction of $C_2H_4:CO:H_2$ (1 : 1 : 1) over Rh-Y. (a) $Rh_6(CO)_{16}/Y$; (b) after exposure of sample (a) to the mixture at 393 K for 5 h; (c) $Rh^I(CO)_2/Y$; (d) after exposure of sample (c) to the mixture at 393 K for 6 h; (e) exposure of Rh-Y pretreated with H_2 at 393 K for 3 h to CO at 393 K for 3 h; (f) after exposure of sample (e) to the mixture at 393 K for 5 h.

hydroformylation. As shown by spectrum (b) in Fig. 4, no appreciable changes were observed on the bands due to $Rh_6(CO)_{16}$. In addition, no bands due to the propionaldehyde formed were observed, indicating that $Rh_6(CO)_{16}$ itself would not be the active species for hydroformylation. This result agrees with that obtained by Rode *et al.* (7). The formation of propionaldehyde during exposure of $Rh_6(CO)_{16}/Y$ to $C_2H_4 + H_2$ (Fig. 3), therefore, would be due to the reaction of $C_2H_2 + H_2$ with CO (from decomposition of $Rh_6(CO)_{16}$) on the active species formed during the exposure. The following result

supports this interpretation. As shown by spectrum (c) in Fig. 3, the sample once exposed to $C_2H_4 + H_2$ showed activity for ethylene hydroformylation, indicating formation of active species during exposure of $Rh_6(CO)_{16}/Y$ to $C_2H_4 + H_2$. On the sample for spectrum (b) in Fig. 3, the color of the sample was found to be gray, while its original color was light yellow.

On the exposure of $Rh^I(CO)_2/Y$ to the reaction mixture, almost no appreciable changes were observed on the bands due to $Rh^I(CO)_2$ as shown by spectrum (d) in Fig. 4. In this case, however, a very small amount of propionaldehyde was formed. The following two cases may possibly account for the formation of propionaldehyde on $Rh^I(CO)_2/Y$. The first is that $Rh^I(CO)_2$ could catalyze hydroformylation with a mixture of $C_2H_4 + CO + H_2$. The second is that the active species were formed during exposure of the sample to the reaction mixture, while the amount of the active species formed was considerably less than that of $Rh^I(CO)_2$.

As shown in Fig. 3 (spectrum (e)), the majority of $Rh^I(CO)_2$ could not interact with $C_2H_4 + H_2$ during exposure of $Rh^I(CO)_2/Y$ to $C_2H_4 + H_2$. Therefore, for evaluation of the ability of $Rh^I(CO)_2$ for ethylene hydroformylation, whether or not all of $Rh^I(CO)_2$ on the sample in spectrum (d) in Fig. 4 could be effectively exposed to the reaction mixture is important. In order to clarify this point, the sample with $Rh^I(CO)_2$ was exposed to a mixture of $C_2H_4 + ^{13}CO + H_2$. The rate of exchange reaction between CO molecules on $Rh^I(CO)_2$ and gaseous CO has already been found to be fast even at 323 K (15, 18). As shown by spectrum (b) in Fig. 5, the bands due to CO shifted to lower values after exposure to the mixture. Evacuation of sample (b) gave spectrum (c), where the pattern of spectrum (c) was almost identical with that of spectrum (a) (wavenumbers shifted from 2115, 2098, 2044, and 2015 to 2065, 2050, 2002, and 1975 cm^{-1} , respectively). Thus, the rate of the exchange reaction was fast at 323 K

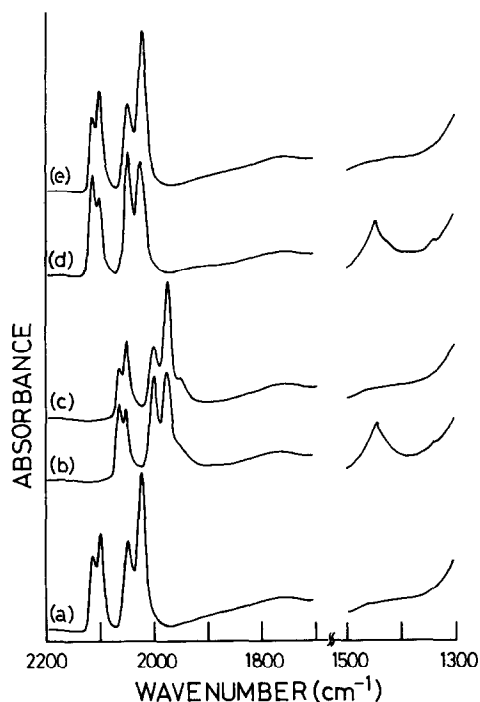


FIG. 5. Exchange reaction of ^{12}CO in $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ with ^{13}CO in a gas mixture of $\text{C}_2\text{H}_4 + ^{13}\text{CO} + \text{H}_2$. (a) $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$; (b) after exposure of sample (a) to $\text{C}_2\text{H}_4 : ^{13}\text{CO} : \text{H}_2$ (1 : 1 : 1) at 323 K for 1 h; (c) sample (b) followed by evacuation at 323 K for 10 min; (d) after exposure of sample (c) to $\text{C}_2\text{H}_4 : ^{12}\text{CO} : \text{H}_2$ (1 : 1 : 1) at 323 K for 1 h; (e) sample (d) followed by evacuation at 323 K for 10 min. Spectra (b) and (d) were recorded in the presence of the gas mixture in gas phase.

even in the presence of $\text{C}_2\text{H}_4 + \text{H}_2$. Replacement of ^{13}CO with ^{12}CO was also fast as shown by spectrum (d) or (e). Comparing spectrum (b) with (c) (or spectrum (d) with (e)), it is clear that the C_2H_4 molecule could coordinate to $\text{Rh}^{\text{I}}(\text{CO})_2$. The corresponding changes also took place at 393 K. These results suggest that $\text{Rh}^{\text{I}}(\text{CO})_2$ on the sample could be effectively exposed to the reaction mixture. If the active species were $\text{Rh}^{\text{I}}(\text{CO})_2$, the rate of propionaldehyde formation should be faster on the sample of spectrum (d) in Fig. 4 than on the sample of spectrum (f) in Fig. 3, because a number of $\text{Rh}^{\text{I}}(\text{CO})_2$ on the former was more than that on the latter. As shown by spectrum (f) in

Fig. 3, however, the sample once exposed to $\text{C}_2\text{H}_4 + \text{H}_2$ became very active for ethylene hydroformylation, and the rate on it was much faster than the rate on the sample of spectrum (d) in Fig. 4. Therefore, $\text{Rh}^{\text{I}}(\text{CO})_2$ itself would not be considered to be the active species as already pointed out by Rode *et al.* (7).

We now discuss the possibility of the second case. It is noteworthy to pay attention to the change in color from light yellow to gray, which was observed during exposure of $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ to the gas mixture for hydroformylation (Fig. 4) as well as during exposure of $\text{Rh}_6(\text{CO})_{16}/\text{Y}$ and $\text{Rh}^{\text{I}}(\text{CO})_2/\text{Y}$ to $\text{C}_2\text{H}_4 + \text{H}_2$. The enhancement of the catalytic activity for hydroformylation seems to always be accompanied by changes of color of the sample from light yellow to gray. The color of the fresh Rh-Y pretreated with hydrogen at 393 K for 3 h was gray. In fact, this sample showed a very high activity for ethylene hydroformylation as shown by spectrum (f) in Fig. 4. The effects of pretreatments on the catalytic activity are consistent with the results of catalytic runs in a flow system at atmospheric pressure (3, 4). As shown in Fig. 6, X-ray photoelectron spectrum of the fresh Rh-Y exposed to H_2 at 393 K showed Rh $3d$ peaks at 311.8 eV (for $3d_{3/2}$) and 307.0 eV (for $3d_{5/2}$). These values agreed well with those for rhodium metal (spectrum (a)). The results obtained in the present work may indicate an important role of metallic rhodium particles as active species for olefin hydroformylation or precursors of them. However, the possibility of $\text{HRh}(\text{CO})_x$ species as the active species, which were directly formed from rhodium species other than metallic rhodium species by the reaction with hydrogen, would not be excluded. Also, the possibility of formation of $\text{HRh}(\text{CO})_x$ species from fine metal particles of rhodium would not be excluded, since fragmentation of fine metal particles of rhodium into $\text{Rh}^{\text{I}}(\text{CO})_2$ species has been shown during exposure of the samples to atmospheres containing CO in several studies on

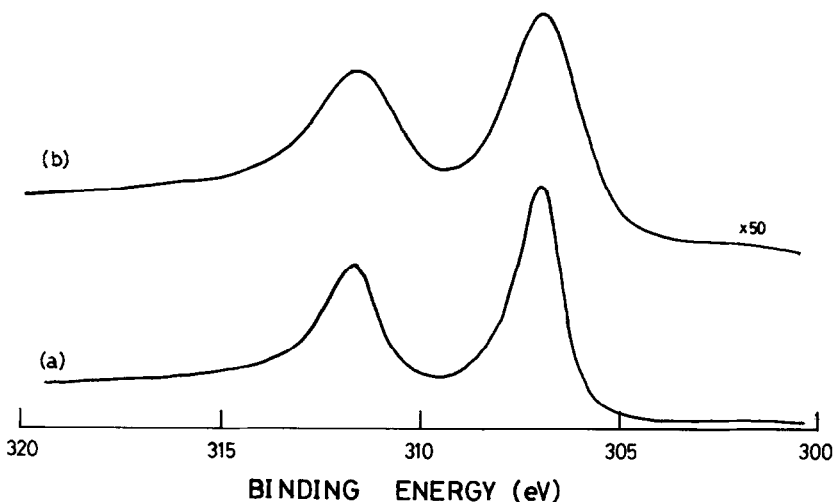


FIG. 6. An XP spectrum of Rh-Y. (a) Rhodium metal; (b) Rh-Y exposed to H_2 at 393 K for 3 h. Binding energy values were referenced to the peak at 284.6 eV for C 1s.

CO-Rh zeolites and CO-Rh/Al₂O₃ systems (8, 19-22).

In conclusion, neither Rh₆(CO)₁₆ species nor Rh^I(CO)₂ species are the active species for olefin hydroformylation themselves as already pointed out by Rode *et al.* (7). The results obtained in the present work clearly showed the important role of hydrogen in the formation of active rhodium species for olefin hydroformylation on the Rh-Y zeolite.

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