April, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1273—1278(1993)* 1273

Unusual Effects of the Reaction Temperature on the Catalytic Activity of Rh/Active-Carbon for Ethylene Hydroformylation

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(Received September 2, 1992)

The apparent activation energies for propionaldehyde and ethane formation from C_2H_4, CO, and H_2 on a Rh/active-carbon catalyst, once used for a reaction at 453 K, were found to be 40 and 76 kJ mol^{-1}, respectively. These values were much lower than those on a fresh Rh/active-carbon catalyst (120 and 125 kJ mol^{-1}). Changes in the apparent activation energies were also induced by exposure of a fresh catalyst to CO at temperatures >433 K. Such catalytic behaviors, however, were not observed on a Rh/silica-gel catalyst. On the fresh Rh/active-carbon catalyst, the amount of adsorbed CO was found to be much more than that of adsorbed H_2. The temperature-programmed desorption spectrum (TPD) of CO on the catalyst exposed to CO at 353 K after an H_2 treatment at 573 K showed a single desorption peak at ca. 470 K; the value for the CO/Rh molar ratio was found to be 2.6. The amount of CO desorbed from the catalyst exposed to CO at 473 K, however, was found to be much less than that on the catalyst exposed to CO at 353 K. Namely, unusual effects of the reaction temperature on the catalytic activities, which were observed on the fresh Rh/active-carbon catalyst, were very closely related to changes in the amount of CO desorbed from the catalyst during TPD runs.

Active carbon has been used as a support in the preparation of supported transition metal catalysts, as well as inorganic oxides, such as SiO_2 and Al_2O_3. In some cases, the catalytic behavior of the catalyst using active carbon as a support has been found to be different from that of a catalyst using an inorganic oxide as the support, e.g., methanol carbonylation over supported rhodium catalysts and nickel catalysts, as reported by Fujimoto et al.[1—3]

It has been reported that ethylene hydroformylation is catalyzed by several heterogeneous rhodium catalysts, such as Rh/zeolites and Rh/SiO_2.[4—13] Rhodium supported on active carbon was also found to be active for ethylene hydroformylation. In this case, however, a considerable amount of 3-pentanone was formed during the reaction, particularly at reaction temperatures lower than 393 K.[14,15] The formation of 3-pentanone has not been observed over the Rh/SiO_2 catalyst. In addition, the apparent activation energy for propionaldehyde formation was found to be ca. 120 kJ mol^{-1} on the Rh/active-carbon catalyst. This value is much higher than that on the Rh/SiO_2 catalyst (ca. 50 kJ mol^{-1}). Thus, the catalytic behavior of Rh/active-carbon for ethylene hydroformylation has been found to be different from that of the Rh/SiO_2 catalyst, not only regarding product distribution, but also regarding the effects of the reaction temperature on the catalytic activity. In the present work, the effects of the reaction temperature on the catalytic activity of Rh/active-carbon for ethylene hydroformylation were studied in detail.

Experimental

The catalysts, Rh/active-carbon and Rh/silica-gel with 2.0 wt%-Rh as a metal (denoted by Rh/AC and Rh/SG, respectively), were prepared by a conventional impregnation method from rhodium trichloride trihydrate (obtained from N. E. Chemcat Corp.) and active carbon (obtained from Wako Pure Chemicals Inc., specific surface area: 930 m^2 g^{-1}) or silica gel (from Nishio Ind., Inc., 420 m^2 g^{-1}).

The apparatus used for ethylene hydroformylation was a fixed-bed type reactor with continuous flow at atmospheric pressure. The standard catalytic run was performed as follows: A catalyst (0.50 g) placed in the reactor was pretreated with hydrogen (50 cm^3(STP) min^{-1}) at 573 K for 3 h, and then cooled below 323 K in a H_2 stream. If necessary, cooling of the catalyst bed below 323 K in a H_2 stream was followed by a treatment with CO at an appropriate temperature for 1 h. In this case, after the sample was cooled in a CO stream below 353 K, the gas stream was changed to a He stream. A reaction mixture of He–C_2H_4(20%)–CO(20%)–H_2(20%) (100 cm^3(STP) min^{-1}) was fed in order to start the reaction; the catalyst bed was then heated to the temperature at which the reaction should be performed. The concentrations of products in the effluent gas stream were determined by gas chromatography.

The amounts of hydrogen or carbon monoxide adsorbed on the catalyst were measured at room temperature by a conventional static method using a glass-made apparatus connected to a vacuum line. The apparatus used for temperature-programmed desorption (TPD) of CO from the catalyst was a conventional flow system operated at atmospheric pressure, as described elsewhere.[16]

Results and Discussion

The reaction of C_2H_4, CO, and H_2 over the Rh/AC catalyst was carried out at 383 K. The main products were found to be propionaldehyde, 3-pentanone, and ethane. The active site for 3-pentanone formation, however, rapidly became deactivated at temperatures >413 K, as previously reported.[14,15] In the present work, attention was focused on the effects of the reaction temperature on the catalytic activities for propionaldehyde and ethane formation. The rates of formation for these two products, denoted by r_{PA} and r_E, respectively, decreased with time on stream, while their changes became small after ca. 70 h (r_{PA} and r_E after 70 h on stream were found to be ca. 60% of those on stream for 10 h). After a reaction at 383 K for 80 h, the reaction temperature was stepwisely increased to 413 K in the sequence 393–403–413 K; the reaction at each temperature was continued until both r_{PA} and r_{E} remained almost unchanged with time on stream (for 20 h). Any catalyst not used for a reaction at temperatures >413 K is called "fresh". The effects of the reaction temperature on r_{PA} and r_{E} over a fresh catalyst are indicated in Fig. 1 by the open circles and squares, respectively. Both r_{PA} and r_{E} on fresh Rh/AC significantly increased with an increase in the reaction temperature from 383 to 413 K. Their apparent activation energies (denoted by E_{PA} and E_{E}) were estimated to be 120 and 125 kJ mol^{-1}, respectively. The reaction at 413 K was followed by a reaction at 453 K for 24 h. After the reaction at 453 K, the temperature was changed in the sequence 423–393–413–403–383–433 K. The values for r_{PA} and r_{E} at 413 K on the catalyst used for the reaction at 453 K were observed to be lower than those on the fresh catalyst (ca. 70 and 60%, respectively), suggesting some deactivation of the active sites during the reaction at 453 K. However, r_{PA} on this catalyst was found to be higher than that on a fresh catalyst at reaction temperatures below 403 K. In the present work, a catalyst once used at 453 K is called "activated". As shown by the full circles, a linear relation between ln (r_{PA}) and $1/T$ was observed on the activated catalyst, where E_{PA} was calculated to be 40 kJ mol^{-1}. Also, a linear relation between ln (r_{E}) and $1/T$ (full squares) with a value of 76 kJ mol^{-1} for E_{E} was observed. Thus, the values for E_{PA} and E_{E} on the activated catalyst were much lower than those on the fresh catalyst. A control experiment on the Rh/SG catalyst was also carried out. As shown in Fig. 2, no appreciable differences (not only in E_{PA} (50 kJ mol^{-1}), but also in E_{E} (87 kJ mol^{-1})) were observed between the fresh Rh/SG catalyst and the catalyst used at 453 K, while both r_{PA} and r_{E} on the latter catalyst were lower than those on the former (ca. 85% for r_{PA} and 75% for r_{E}). Thus, the catalytic behavior of the Rh/AC catalyst was found to be very different from that of the Rh/SG catalyst.

The enhancement in r_{PA} and r_{E} observed on Rh/AC at reaction temperatures <403 K would be due to an increase in the number of active sites and/or changes in the nature of the active sites. If the latter is the main reason, the considerable difference in the apparent activation energies between fresh and activated catalysts means that the reaction mechanism on the former is different from that on the latter. In this case, the reaction orders of r_{PA} and r_{E} with respect to the three reactants on the fresh catalyst should be observed to be different from those on the activated catalyst. The effects of the partial pressure of the reactants on r_{PA} and r_{E} are summarized in Table 1, when the rate is expressed by the following power-law:

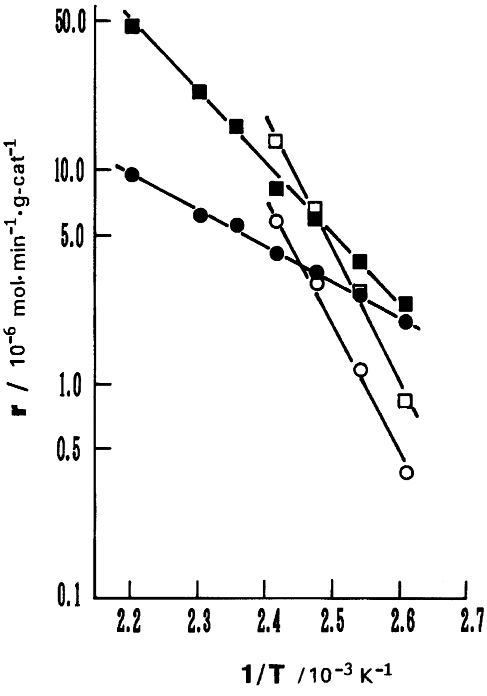

Fig. 1. Effects of the reaction temperature on the catalytic activities of the Rh/active-carbon catalyst-I. (○, □: r_{PA} and r_{E} on the fresh Rh/AC catalyst, respectively; ●, ■: r_{PA} and r_{E} on the activated Rh/AC catalyst, respectively).

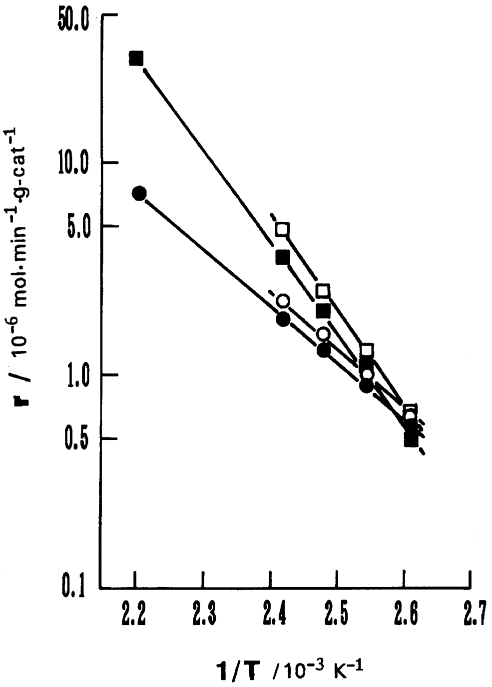

Fig. 2. Effects of the reaction temperature on the catalytic activities of the Rh/silica-gel catalyst. (○, □: r_{PA} and r_{E} on the fresh Rh/SG catalyst, respectively; ●, ■: r_{PA} and r_{E} on the Rh/SG catalyst used for the reaction at 453 K, respectively).

Table 1. Partial Pressure Dependencies of the Reaction Rates on Three Reactants[a)]

Catalyst	Rate	C_2H_4 l	H_2 m	CO n
"fresh"	r_{PA}	0.8	1.0	−1.0
	r_E	0.9	0.9	−1.2
"activated"	r_{PA}	0.8	1.0	−0.8
	r_E	0.8	0.8	−1.1

a) l, m, n, : reaction orders in a power-low form rate expression, $r=kP_{C_2H_4}{}^{l}P_{H_2}{}^{m}P_{CO}{}^{n}$.

$$r = k\ P_{C_2H_4}{}^{l}\ P_{H_2}{}^{m}\ P_{CO}{}^{n}. \tag{1}$$

Almost no appreciable differences in the reaction orders were observed between fresh and activated catalysts, suggesting that no important differences exist between the nature of the active sites on both catalysts. Therefore, the enhancement in the catalytic activities observed on the fresh Rh/AC catalyst would be attributed to an increase in the number of active sites, rather than changes in the nature of the active sites.

In order to clarify whether the change in the number of active sites was reversible or irreversible at temperatures below 403 K, catalytic runs in which the reaction temperature was programmed as 373–383–393–403–393–373–383 K were carried out. If the changes were irreversible, E_{PA} and E_E after a reaction at 403 K should be observed to be the same as those on the activated Rh/AC catalyst. As shown in Fig. 3, E_{PA} and E_E after a reaction at 403 K were observed to be 92 and 105 kJ mol^{-1}, respectively. These values are much higher than those on an activated catalyst, suggesting that the change induced at temperatures <403 K was mainly reversible, whereas the process was to some degree irreversible.

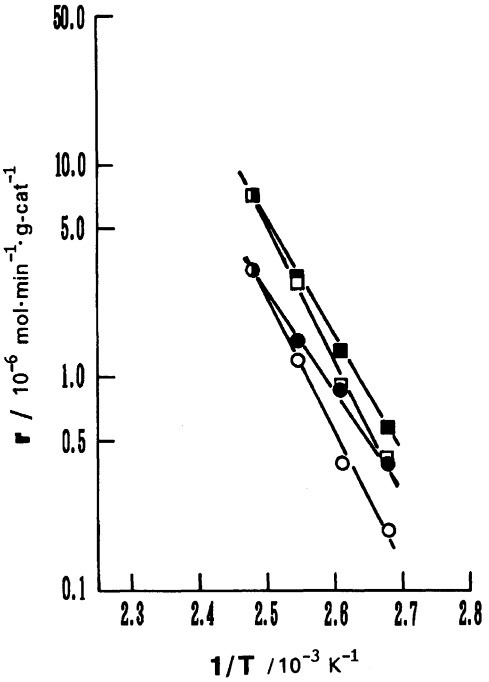

Fig. 3. Effects of the reaction temperature on the catalytic activities of the Rh/active-carbon catalyst-II. (○, □ : r_{PA} and r_E on the fresh Rh/AC catalyst, respectively; ●, ■ : r_{PA} and r_E on the catalyst once used for the reaction at 403 K, respectively).

One of the possible explanations for the increase in the number of active sites on the fresh Rh/AC catalyst may be a removal of by-products with higher boiling points than propionaldehyde from the catalyst. In ethylene hydroformylation over the Rh/AC catalyst, the formation of 3-pentanone was observed. Also, a very small amount of 2-methyl-2-pentenal was formed during the reaction. The accumulation of such nonvolatile by-products on the catalyst might induce some inhibition through physical pore blockage and/or chemical coordination to the active sites. If the process for the (removal)–(accumulation) of by-products was reversible on the fresh catalyst and was irreversible on the activated catalyst, E_{PA} and E_E on the catalyst after a reaction at 403 K would be observed to be close to the values on the fresh catalyst, as observed in Fig. 3. During a reaction at 393 K, 3-pentanone (about twice the amount of that formed by the reaction) or 2-methyl-2-pentenal (a comparable amount to the 3-pentanone formed) was introduced into the system. Not only on the fresh catalyst, but also on the activated catalyst, however, no appreciable effects of such nonvolatile compounds on r_{PA} and r_E were observed. Namely, activation of the fresh Rh/AC catalyst could not be explained by the effects of such nonvolatile products as 3-pentanone or 2-methyl-2-pentenal.

The changes in the number of active sites on the fresh Rh/AC catalyst might be induced by exposure of the catalyst to the reaction gas mixture. No appreciable enhancement in r_{PA} and r_E was observed when the catalyst was exposed to C_2H_4 at 433 K. On the other hand, exposure of the catalyst to CO at temperatures higher than 433 K enhanced both of the activities, as shown by Runs 4 and 5 (Table 2); however, exposure at 353 K (Run 2) or at 393 K (Run 3) rather reduced them. In the region of reaction temperatures lower than 403K, the apparent activation energies for r_{PA} and r_E on the Rh/AC once exposed to CO at 473 K were found to be 40 and 70 kJ mol^{-1}, respectively. These values almost agreed with those on the activated Rh/AC catalyst. The effects of the treatment with CO on r_{PA} and r_E for Rh/SG are shown by Runs 7—11 in Table 2. The activities on the Rh/SG decreased with an increase in the temperature for the CO treatment. The absence of any positive effects due to a CO treatment on the Rh/SG catalyst corresponds to an absence of the unusual effects of the reaction temperature on the catalytic activities on it. These results clearly show that the changes in r_{PA} and r_E observed on the fresh Rh/AC catalyst during a reaction was induced by exposure of

Table 2. Effects of the CO Treatment of the Catalyst on the Catalytic Activities

Run	Catalyst	CO treatment temperature[a)]	Activity[b)]/10^{-6} mol min^{-1} g-cat^{-1}		
		K	r_{PA}	r_{DEK}	r_E
1	Rh/AC	None	2.0	0.8	4.5
2		353	1.0	0.8	2.6
3		393	1.0	0.8	2.6
4		433	3.9	0.7	5.9
5		473	6.2	0.4	6.6
6[c)]		473	6.2	0.3	6.5
7	Rh/SG	None	1.6	—[d)]	2.3
8		353	1.6	—	2.3
9		393	1.5	—	2.1
10		433	1.3	—	1.8
11		473	1.0	—	1.6

a) All catalysts were pretreated with H_2 at 573 K for 3 h before the exposure to CO (for 1 h). b) Activities were evaluated by r_{PA}, r_{DEK}, and r_E at time on stream of 10 h (reaction temperature: 393 K). c) The CO treatment at 473 K was followed by the treatment with H_2 at 573 K for 1 h. d) Formation of 3-pentanone was not observed.

the catalyst to CO in the reaction gas mixture.

In order to clarify the changes induced by CO on the Rh/AC catalyst, the following experiments were carried out. The adsorption of H_2 or CO on the Rh/AC catalyst was compared with that on the Rh/SG catalyst. Typical adsorption isotherms for H_2 and CO are shown in Fig. 4. In the present work, the amount of H_2 or CO required for a monolayer coverage (q_m) was evaluated by extrapolating a linear part of an adsorption isotherm to the zero of the equilibrium pressure for adsorption. On the Rh/SG catalyst, the values for q_m were obtained as 66×10^{-6} mol/g-cat for H_2 and 148×10^{-6} mol/g-cat for CO, respectively. The ratio of $q_m(CO)/q_m(H_2)$ is 2.2, suggesting that the normal adsorption of H_2 and CO to surface rhodium atoms on the metal particles (each surface rhodium atom can adsorb one H atom or one CO molecule) is predominant on the Rh/SG catalyst. On the Rh/AC catalyst, the values for q_m were obtained as 27×10^{-6} mol/g-cat for H_2 and 250×10^{-6} mol/g-cat for CO, respectively. The steep slope for CO adsorption on the Rh/AC catalyst, however, suggests that the duration of the CO adsorption measurement (10 min) at each point in the figure was insufficient to attain the adsorption equilibrium. Although the value of $q_m(CO)$ estimated from the isotherm would be lower than the value for the true q_m, the ratio of $q_m(CO)/q_m(H_2)$ (9.3) is found to be much greater than that on the Rh/SG catalyst.

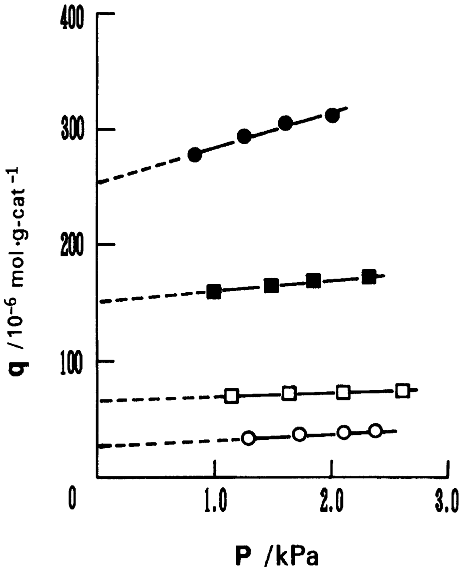

Fig. 4. Adsorption isotherms of H_2 and CO on the Rh/AC catalyst and the Rh/SG catalyst. (○, ●: H_2 and CO adsorption on the Rh/AC catalyst, respectively; □, ■: H_2 and CO adsorption on the Rh/SG catalyst, respectively).

To determine the amount of CO adsorbed on the catalyst and to clarify what kinds of Rh–CO species were formed, a temperature-programmed desorption (TPD) technique was applied. Pretreatments of samples for TPD runs were essentially the same as those for the catalytic runs, i.e., the treatment with H_2 at 573 K for 3 h was followed by a treatment with CO at appropriate temperatures for 1 h. Typical TPD patterns of the CO obtained from the catalyst treated with CO at different temperatures are shown in Fig. 5. The desorption of a small amount of CO_2 was observed during TPD runs. However, it was the same level as that on the active carbon support, itself. In case of a CO treatment at 353 K, the desorption of CO became remarkable at around 400 K, and a single peak was observed at ca. 470 K. The amount of desorbed CO was estimated to be 500×10^{-6} mol/g-cat (CO/Rh=2.6). On the other hand, the amount of desorbed CO from the catalyst with a CO treatment at 473 K (cooled in CO atmosphere to 353 K) (ca. 30×10^{-6} mol/g-cat) was found to be considerably lower than that on the catalyst treated at 353 K, as shown in Fig. 5. The decrease in the amount of CO

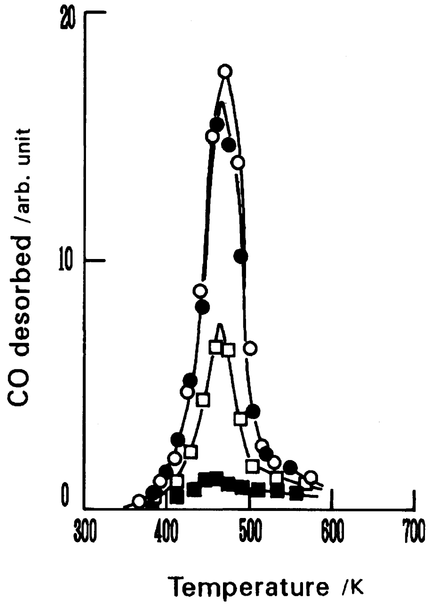

Fig. 5. TPD spectra of CO from a catalyst treated with CO at different temperatures. (○, treated with CO at 353 K; ●, at 393 K; □, at 433 K; ■, at 473 K).

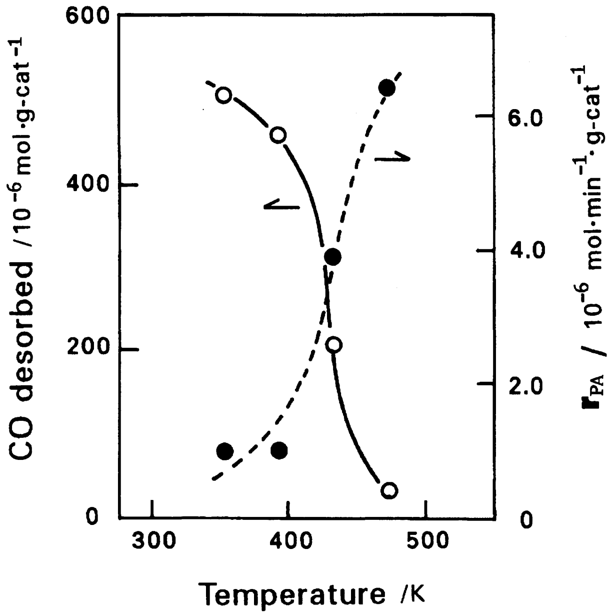

Fig. 6. Effects of the temperature for a CO treatment on the amount of CO desorbed from the catalyst and on r_{PA} (○, CO desorbed; ●, r_{PA}).

desorbed would not be due to an elimination of the Rh component from the catalyst as a result of the formation of volatile Rh–CO complexes, since no appreciable formation of such volatile complexes was observed during exposure of the sample to CO at 353—473 K. The effects of the temperature for the exposure of the catalyst to CO on the amount of CO desorbed during the TPD run are shown in Fig. 6. The amount of CO desorbed decreased along with an increase in the temperature for the CO treatment, particularly notable at around 413 K.

The peak position for CO desorption observed is very close to that observed on the $Rh_6(CO)_{16}$ species formed in Rh/Y-zeolite, where the desorption of CO from the geminal dicarbonyl species, $[Rh(CO)_2]^+$ was observed at ca. 570 K.[16] In fact, we have recently reported that the predominant Rh species on a Rh/AC sample exposed to CO at 353 K was found to be $Rh_6(CO)_{16}$-like species by means of EXAFS.[17] We have also shown that the $Rh_6(CO)_{16}$-like species formed was transformed into metal particles of rhodium at 473 K, even in the presence of CO. Therefore, the desorption of CO from the sample shown in Fig. 5 corresponds to the desorption from $Rh_6(CO)_{16}$-like species on the sample, and the decrease in the amount of CO desorbed (shown in Figs. 5 and 6) reflects the decrease in the amount of $Rh_6(CO)_{16}$-like species present on the sample. As shown in Fig. 6 (or Table 2), r_{PA} remarkably increased when the catalyst was exposed to CO at temperatures of around 413 K. Thus, a transformation of $Rh_6(CO)_{16}$-like species into rhodium metal particles would be responsible for the increase in the catalytic activities. In ethylene hydroformylation over Rh/Y-zeolite, the $Rh_6(CO)_{16}$ species, itself, was found to be inactive for the reaction.[18]

As shown by Run 6 in Table 2, the catalyst treated with H_2 at 573 K after a CO treatment at 473 K, kept its high catalytic activities, thus suggesting that the active sites formed during exposure to CO were stable against the H_2 treatment. On this sample, the amount of CO adsorbed was found to be 66×10^{-6} mol/g-cat. This value corresponds to 34% of Rh-dispersion. Although one important role of fine metal particles of rhodium in ethylene hydroformylation has been suggested,[13,18] we have not observed any strong relation between Rh dispersion and the catalytic activities on the Rh/AC system. It seems to be important to clarify the particle size distribution of Rh on the active carbon support in order to further discuss the catalytic activities in terms of the Rh dispersion.

In conclusion, we have found that changes in the catalytic activities for ethylene hydroformylation and hydrogenation, accompanying considerable decreases in the apparent activation energies, were induced by the exposure of the fresh Rh/active-carbon catalyst to carbon monoxide at temperatures higher than 413 K. These effects were also induced by CO in the reaction gas mixture during ethylene hydroformylation over the fresh Rh/AC catalyst, resulting in the unusual effects of the reaction temperature on the catalytic activities. The enhancement in the catalytic activities has been found to be closely related to the transformation of $Rh_6(CO)_{16}$-like species into metal particles of Rh on the active-carbon support.

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