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## Highly Dispersed Rhodium on Alumina Catalysts: Influence of the Atmosphere on the State and Dispersion of Rhodium

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The state and dispersion of a highly dispersed Rh/Al<sub>2</sub>O<sub>3</sub> catalyst in various reactive atmospheres were investigated by low-temperature infrared spectroscopy of chemisorbed CO. Rh metal particles disintegrate in the presence of CO, and Rh<sup>+</sup> species form as a result of oxidation by surface -OH groups at temperatures  $\lesssim 300$  K. The predominant oxidation process at higher temperatures is presumably related to the dissociative chemisorption of CO. The rates of these processes are strongly dependent on the initial reduction conditions, being less for the more severely reduced samples containing the larger Rh metal particles. A cyclic process of CO adsorption and H<sub>2</sub> reduction leads to particle growth and increasing resistance of the larger particles to disintegration and oxidation in CO. Simultaneous exposure of the samples to CO and H<sub>2</sub> does not prevent the oxidative conversion of some of the Rh<sup>0</sup> into Rh<sup>+</sup> at temperatures  $\geq 473$  K, but complete conversion of the Rh<sup>0</sup> is hindered because the CO ligands are removed by reaction with the H<sub>2</sub>. Water vapor in the presence of CO assists the formation of Rh<sup>+</sup> species.

### Introduction

One of the most effective methods of characterization of highly dispersed metals on supports is infrared spectroscopy of adsorbed CO. Supported rhodium catalysts have been investigated many times with this method,<sup>1-4</sup> beginning with the work of Yang and Garland.<sup>5</sup> Geminal [Rh<sup>+</sup>(CO)<sub>2</sub>], linear [Rh(CO)], and bridging [Rh<sub>x</sub>(CO)] species have been detected<sup>1-5</sup> with other minor species.<sup>1,3</sup> The geminal Rh<sup>+</sup>(CO)<sub>2</sub> species has drawn wide attention,<sup>4</sup> the mechanism of its formation on reduced catalysts being a subject of continuing controversy.<sup>1,4,6</sup>

The formation of Rh<sup>+</sup> from Rh<sup>0</sup> dispersed on Al<sub>2</sub>O<sub>3</sub> during CO adsorption at temperatures  $> 193$  K was attributed by Primet<sup>1</sup> to dissociation of CO



(where the subscript s refers to surface species). Other authors, as reviewed elsewhere,<sup>4</sup> have instead attributed the formation of Rh<sup>+</sup> to the occurrence of the water gas shift reaction. Both interpretations are unsatisfactory in light of several recent experimental observations: (1) the dissociation of CO on Rh/Al<sub>2</sub>O<sub>3</sub> occurs only at temperatures  $> 473$  K,<sup>7</sup> and this dissociation occurs on the (111) face of single-crystal Rh at temperatures  $> 870$  K under ultra-high-vacuum conditions;<sup>8-10</sup> (2) CO<sub>2</sub>, a product of the water gas shift reaction, is adsorbed only weakly on Rh<sup>0</sup> at temperatures  $\leq 300$  K;<sup>11</sup> and (3) mass spectrometric analysis of the gas phase during adsorption of CO on Rh/Al<sub>2</sub>O<sub>3</sub> at 300 K gave evidence of no compounds other than CO.<sup>4</sup>

In the search for alternative interpretations, Hyde et al.<sup>12</sup> proposed a model according to which electrons are pumped off the Rh<sup>0</sup> atoms by the support so that Rh having a partial positive charge is formed. Solymosi and Paszto<sup>4</sup> pointed out that this model might be considered valid for the formation of Rh<sup>+</sup> in a sample such as Rh/Al<sub>2</sub>O<sub>3</sub>, for which the electron work function<sup>13</sup> ( $\phi_e$ ) of the metal (4.98 eV) is lower than that of the support (5.3 eV); however, the model would fail for samples such as Rh/TiO<sub>2</sub>

( $\phi_e$  of reduced TiO<sub>2</sub> = 4.6 eV<sup>14</sup>) and Rh/SiO<sub>2</sub>, for which the work function of the support is lower than that of the metal. Moreover, a recent infrared investigation<sup>15</sup> of CO adsorption on supported Rh has shown that the stretching parameter  $k(\text{CO})$  calculated from the frequencies of the geminal Rh<sup>+</sup>(CO)<sub>2</sub> species is greater when the support is TiO<sub>2</sub> rather than Al<sub>2</sub>O<sub>3</sub>; this result suggests that there is less back donation of electrons from the adsorption site to the ligands on TiO<sub>2</sub>. This result contradicts the fact<sup>14</sup> that the electron work function of reduced titania is lower than that of the supported Rh; the reverse would be expected to occur. We infer that the support contribution to the state and reactivity of supported Rh is not simply the result of electronic interactions.

Numerous recent investigations of supported Rh catalysts have led to new interpretations of the CO-assisted generation of surface Rh<sup>+</sup> sites. Solymosi and Pászto<sup>4</sup> suggested a twofold effect of CO on the surface state of Al<sub>2</sub>O<sub>3</sub>-supported Rh: On the one hand, CO adsorption is supposed to disrupt Rh aggregates at temperatures between 300 and 423 K, since Rh-CO bond energy (185

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$\text{kJ mol}^{-1}$ ) is greater than the Rh–Rh bond energy ( $44.5 \text{ kJ mol}^{-1}$ ),<sup>6</sup> oxidation may then occur through surface –OH groups of the support according to a reaction similar to that proposed by van't Blik et al.<sup>6</sup>



On the other hand, CO adsorption at higher temperatures ( $>448 \text{ K}$ ) has been suggested to assist the nucleation of  $\text{Rh}^0$  crystallites at the expense of isolated  $\text{Rh}^+$  ions. CO has been suggested to play a role in the reduction of  $\text{Rh}^+$  to  $\text{Rh}^0$  and to assist in the sintering of the metal.

The present paper is concerned with the CO-assisted interconversion reactions of Rh dispersed on  $\gamma\text{-Al}_2\text{O}_3$ . This subject has a bearing on the catalytic chemistry of a number of technologically important reactions of CO,<sup>14,16</sup> since activity and selectivity depend on the dispersion of the metal and on the relative amounts of metallic and ionic species. We present results of an infrared spectroscopic investigation of the influence of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  on rhodium carbonyl species formed as a result of CO adsorption on fresh and regenerated catalyst samples. CO adsorption was carried out in various atmospheres in the temperature range 77–773 K; emphasis was placed on the range below room temperature, which has received little attention in the past.

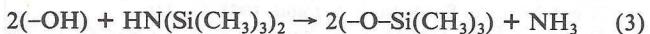
### Experimental Methods

**Catalyst Preparation.** The catalyst samples were prepared by the ion-exchange technique with aqueous  $\text{Rh}(\text{NO}_3)_3$ , as described elsewhere.<sup>17</sup> The  $\gamma\text{-Al}_2\text{O}_3$  support (Conoco) had a BET surface area of  $190 \text{ m}^2 \text{ g}^{-1}$ ; the metal loading was 0.7 wt % Rh.

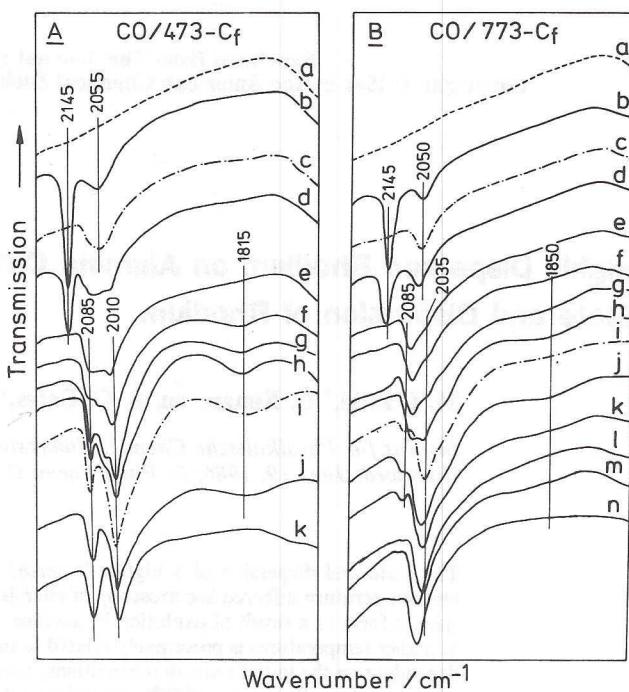
**Fresh Catalyst.** Fresh samples of rhodium supported on  $\gamma\text{-Al}_2\text{O}_3$  samples were obtained by in situ heating of self-supporting wafers ( $20 \pm 2 \text{ mg cm}^{-2}$ ) of the  $\text{Rh}(\text{NO}_3)_3$ -impregnated  $\gamma\text{-Al}_2\text{O}_3$  in a stream of dry  $\text{H}_2$  ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) at 473 and 773 K (heating rate  $10 \text{ K min}^{-1}$ ) for 1 h. The temperature was then lowered to 298 K and the sample cooled to 77 K in  $\text{H}_2$ .  $\text{H}_2$  was pumped off ( $10^{-5} \text{ Torr}$ ) at 77 K for 30 min. These samples are designated 473-C<sub>f</sub> and 773-C<sub>f</sub>, respectively, where the C<sub>f</sub> refers to fresh catalyst. A complete desorption of  $\text{H}_2$  is not expected under these conditions. The retained hydrogen may enhance surface mobility of  $\text{Rh}^0$  upon exposure to CO at temperatures above 473 K.<sup>18</sup>

**Treatment Gases.**  $\text{H}_2$ ,  $\text{O}_2$ , and CO supplied by Linde (West Germany) had nominal purities of 99.99%.  $\text{H}_2$  and CO were further purified by passage through the appropriate Oxisorb traps;  $\text{O}_2$  was passed through a trap containing molecular sieve 4A (Merck) for drying. Doubly distilled water, deaerated by evacuation during freeze-thaw cycles, was the source of the water vapor at 298 K. 1,1,1,3,3-Hexamethyldisilazane (HMDS) was provided by Aldrich and had a purity of 99%. It was deaerated by evacuation during freeze-thaw cycles.

**Catalyst Dehydroxylation.** Fresh catalyst samples (473-C<sub>f</sub>) were partially dehydroxylated, either by evacuation ( $10^{-5} \text{ Torr}$ ) at 473 K for 1 h or by treatment with HMDS. This treatment was carried out (in situ) by a procedure analogous to that described by Van Roosmalen et al.<sup>19</sup> as HMDS vapor at 5 Torr reacted with a freshly prepared catalyst wafer (after pumping off of the  $\text{H}_2$  atmosphere) at 473 K for 1 h. The wafer was degassed at the same temperature and for the same time, and the temperature was then reduced to 298 K. HMDS reacts readily with hydroxyl groups, which are weak Brønsted acids, leading to the formation of stable silyl ethers:<sup>20</sup>



HMDS is a nitrogen base that can also coordinate to Lewis acid sites. The resulting surface complexes are evidently less stable (decomposing at room temperature<sup>21</sup>) than the silyl ethers (which



**Figure 1.** Infrared spectra of CO adsorbed on catalyst samples 473-C<sub>f</sub> (A) and 773-C<sub>f</sub> (B). The spectra were taken after in situ exposure to 40 Torr of CO for 5 min at 77 (b), 100 (d), 180 (e), 230 (f), 270 (g), and 298 K (h), and for 20 min at 373 (j), 473 (k), 573 (l), 673 (m), and 773 K (n). Also shown are the catalyst background spectrum (a) and the spectrum obtained after evacuation at  $10^{-5} \text{ Torr}$  at 77 (c) and 298 K (i) for 5 min.

decompose at temperatures  $\geq 930 \text{ K}$ ). The partially dehydroxylated catalyst samples are designated PDH [e.g., 473-C<sub>f</sub> (PDH)] to distinguish them from the hydroxylated ones.

**Catalyst Regeneration.** Catalyst sample 473-C<sub>f</sub>, used in high-temperature CO adsorption experiments (i.e., at temperatures up to 473 K) was regenerated by heating (in situ) in a static atmosphere (1 atm) of  $\text{H}_2$  at 473 K for 1 h, during which the  $\text{H}_2$  dose was replenished at 20-min intervals (i.e., twice), followed by degassing at 473 K for 20 min before the temperature was lowered to 298 K. The resulting sample is designated 473-C<sub>n</sub>, where  $n$  is the number of regenerations undergone by the sample. Thus 473-C<sub>2</sub> indicates a sample doubly regenerated at 473 K.

**CO Adsorption.** Experiments characterizing CO adsorption at 77–773 K on various catalyst samples were carried out in situ in a low-temperature infrared cell equipped with  $\text{CaF}_2$  windows; the cell design<sup>23</sup> and adsorption procedure<sup>24</sup> are described elsewhere.

**Infrared Spectra.** Spectra of adsorbed CO in the range 1700–2300  $\text{cm}^{-1}$  were recorded at a resolution of  $5.3 \text{ cm}^{-1}$  with a Perkin-Elmer 580B spectrophotometer. The wavenumber accuracy was better than  $\pm 2 \text{ cm}^{-1}$ .

### Results and Discussion

**CO Adsorption on Fresh Catalyst Samples.** Infrared spectra of CO adsorbed on the samples 473-C<sub>f</sub> and 773-C<sub>f</sub> at 77–773 K are shown in parts A and B of Figure 1, respectively. The adsorption at 77 K gave rise to spectra b in these figures, which include strong, symmetric bands at  $2145 \text{ cm}^{-1}$  and broad bands centered around  $2050$ – $2055 \text{ cm}^{-1}$ . The high-frequency bands disappeared, either upon degassing at 77 K (spectra c) or as a result of increasing the CO adsorption temperature to  $\geq 180 \text{ K}$  (spectra e). This behavior, together with the occurrence of the

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band at a frequency close to that ( $2143\text{ cm}^{-1}$ ) of the CO stretching band of gas-phase CO, indicates that the carbonyl species are not significantly perturbed by the surface. Beebe et al.<sup>25</sup> distinguished two different types of CO species weakly held at 77 K, namely, CO molecules hydrogen bonded to surface  $-\text{OH}$  groups ( $2150\text{--}2160\text{ cm}^{-1}$ ) and others physisorbed through weak van der Waals forces ( $2135\text{--}2145\text{ cm}^{-1}$ ). Consequently, we infer that under our conditions the physisorbed species prevail. The spectra in the O-H stretching region indicated strongly perturbed  $-\text{OH}$  groups, which we associate with lateral interactions of neighboring groups via hydrogen bonds on the strongly hydroxylated  $\gamma\text{-Al}_2\text{O}_3$  surface. The absence of hydrogen-bonded carbonyl species suggests that lateral interactions between neighboring  $-\text{OH}$  groups are energetically more favorable than hydrogen bonds with CO.

The bands still observed at  $2050\text{--}2055\text{ cm}^{-1}$  after degassing of the sample at 77 K are therefore inferred to originate from more firmly held CO species. This band is observed at a frequency much lower than the range ( $2190\text{--}2244\text{ cm}^{-1}$ ) over which  $\text{Al}^{3+}(\text{CO})$  species are usually encountered.<sup>26,27</sup> Consequently, Rh atoms are inferred to be the most probable adsorption sites for these carbonyls, which are assigned as linear  $\text{Rh}(\text{CO})$  species.<sup>1-4</sup> The greater width of the band characterizing the 473-C<sub>f</sub> sample (spectrum c, Figure 1A) suggests that the Rh aggregates involved are more highly dispersed on the former sample. Transmission electron microscopy of a sample reduced at 473 K did not indicate any Rh aggregates having diameters larger than 0.8 nm, and the sample reduced at 773 K did indeed show a slightly larger average particle size. This result agrees with Primet's<sup>1</sup> calculations of Rh sizes from the broadening of characteristic X-ray diffraction lines of Rh in similarly prepared catalysts, which indicated larger Rh particles ( $\geq 2\text{ nm}$ ) in the catalyst prepared by reduction at high temperatures ( $\geq 773\text{ K}$ ) than in the catalyst prepared at 473 K ( $\leq 1\text{ nm}$ ). We emphasize that the spectra of CO adsorbed at 77 K clearly demonstrate the absence of any oxidized Rh sites. Therefore, the catalyst was originally in a fully reduced state, an observation that had been reported by others.<sup>28,29</sup>

Spectra d-n in Figure 1A,B show significant changes in the infrared absorption with increasing temperature of the CO adsorption. The extent of these changes depends strongly on the reduction conditions and, hence, on the particle size. CO adsorption on the 473-C<sub>f</sub> sample at temperatures up to 298 K (spectra d-h, Figure 1A) leads to a modification of the simple band at  $2055\text{ cm}^{-1}$ , with additional components appearing at  $2010$  and  $2085\text{ cm}^{-1}$ ; another broad absorption develops simultaneously at about  $1815\text{ cm}^{-1}$ .

These changes in the spectrum suggest<sup>2</sup> the formation of the geminal  $\text{Rh}^+(\text{CO})_2$  (bands at  $2010$  and  $2085\text{ cm}^{-1}$ ) and of bridging  $\text{Rh}_x(\text{CO})$  (band at  $1815\text{ cm}^{-1}$ ) species, which implies that the formation of  $\text{Rh}^+$  sites commences at a temperature (100 K, spectrum d, Figure 1A) much lower than that (193 K) observed by Primet.<sup>1</sup> Since the dissociation of CO on  $\text{Rh}/\text{Al}_2\text{O}_3$  has been excluded<sup>7</sup> at temperatures  $< 473\text{ K}$ , we consider the oxidative mechanism proposed by van't Blik et al.<sup>6</sup> and adopted by Solymosi and Paszto<sup>4</sup> to account for the formation of the  $\text{Rh}^+$  sites. The following overall surface reaction is postulated:



Surface  $-\text{OH}$  groups are the likely oxidizing agent for the  $\text{Rh}^0$ .

The infrared spectra reported by Primet<sup>1</sup> for adsorption of CO on  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$  at temperatures below 300 K (the only such low-temperature spectra in the literature) show that adsorption at 77 K gave rise to absorptions at  $2190$  and  $2160\text{ cm}^{-1}$  in addition to the absorptions mentioned above that are diagnostic of  $\text{Rh}(\text{CO})$

and  $\text{Rh}_x(\text{CO})$  species. As stated above, the absorptions at  $2190$  and  $2160\text{ cm}^{-1}$  are characteristic of the formation of  $\text{Al}^{3+}\text{-CO}^{26}$  and hydrogen-bonded CO surface species,<sup>25</sup> respectively. The formation of these species clearly indicates a low hydroxyl group content on the surface of Primet's sample that was prepared at 773 K and then degassed at 298 K for 1 h. We infer that the comparatively high surface hydroxyl group content of our sample 473-C<sub>f</sub> could explain the CO-assisted formation of the  $\text{Rh}^+$  sites at lower temperatures. On the other hand, the low-temperature formation of  $\text{Rh}^+$  assisted by the hydroxyl groups may simultaneously explain the retardation of Rh particle growth (probably by reduction of the surface mobility of Rh), which becomes observable (as indicated by the band at  $1815\text{ cm}^{-1}$ ) in our sample at temperatures ( $\geq 230\text{ K}$ ) much higher than that (77 K) indicated by the results of Primet.<sup>1</sup>

After evacuation of the sample at 298 K, the predominant carbonyl species was  $\text{Rh}^+(\text{CO})_2$ , as indicated by bands at  $2085$  and  $2010\text{ cm}^{-1}$  (spectrum i, Figure 1A). We infer that the  $\text{Rh}(\text{CO})$  species was not completely eliminated, since the twin bands that characterize the geminal species are still not completely resolved in the spectrum. When the temperature of the CO adsorption was increased to 373 (spectrum j) and then to 473 K (spectrum k), the twin bands become well resolved, and the band at about  $1815\text{ cm}^{-1}$  disappeared, indicating the abundance of the geminal species ( $\text{Rh}^+$  sites) and the almost complete elimination of the linear and bridging species indicative of  $\text{Rh}^0$  sites. This is a striking result; we infer that the conversion of  $\text{Rh}^0$  into  $\text{Rh}^+$  is most likely the result of the initiation of an additional oxidative mechanism at the higher temperatures. As reviewed above, the dissociation of CO on  $\text{Rh}/\text{Al}_2\text{O}_3$  at temperatures  $\geq 473\text{ K}$  is quite possible; the oxygen released may be involved in the surface oxidation of  $\text{Rh}^0$  at 473 K.

Contrasting results were obtained with the sample initially reduced in  $\text{H}_2$  at the higher temperatures (773 K). Spectra e-h of Figure 1B indicate the formation of the geminal species (weak absorptions at  $2085$  and  $2035\text{ cm}^{-1}$ ); however, the linear species remained dominant, as indicated by the strong absorption at  $2070\text{ cm}^{-1}$ . Small proportions of the bridging species were also present, as indicated by weak absorption centered around  $1850\text{ cm}^{-1}$ . These observations suggest that the oxidation of  $\text{Rh}^0$  is more strongly retarded on the sample reduced at 773 K than on the sample reduced at 473 K. This result is attributed to the greater size of the Rh particles on the former sample and possibly also to the higher degree of dehydroxylation of the  $\text{Al}_2\text{O}_3$  surface at the higher reduction temperature. We infer that the CO-assisted process that leads to disruption of the Rh particles preceding the oxidation is much slower on the larger particles. The absorption indicative of the  $\text{Rh}_x(\text{CO})$  species formed on the sample reduced at 773 K (Figure 1B) occurs at a frequency ( $1850\text{ cm}^{-1}$ ) higher than that ( $1815\text{ cm}^{-1}$ ) indicative of the  $\text{Rh}_x(\text{CO})$  species on the sample reduced at 473 K (Figure 1A); the band location is correlated with the Rh particle size.

Spectra j and k of Figure 1B indicate a slight enhancement in the formation of the  $\text{Rh}^+(\text{CO})_2$  species with an increase in the CO adsorption temperature to 373 and 473 K, respectively. Although the CO dissociation is possible at 473 K, the amount of the oxidatively formed  $\text{Rh}^+$  monitored by the CO adsorption at 473 K (spectrum k) is still much less than that for the sample reduced at 473 K (spectrum k, Figure 1A). This result confirms the strong dependence of the oxidative conversion of  $\text{Rh}^0$  to  $\text{Rh}^+$  on the initial Rh particle size.

CO adsorption at still higher temperatures (573–773 K) on the sample reduced at 773 K gave rise to spectra (l-n of Figure 1B) demonstrating a marked erosion of the absorptions indicative of the geminal and bridging carbonyl species. At 773 K, spectrum n displays solely the absorption diagnostic of the linear species at  $2055\text{ cm}^{-1}$ . These spectral modifications may indicate the abundance of either highly dispersed  $\text{Rh}^0$  sites or, alternatively, large aggregates covered with carbon. The latter assumption would be in harmony with results of Yates et al.,<sup>18</sup> who observed that CO adsorption enhances the surface mobility of  $\text{Rh}^0$  in the presence of a  $\text{H}_2$  atmosphere at temperatures  $> 473\text{ K}$ . According

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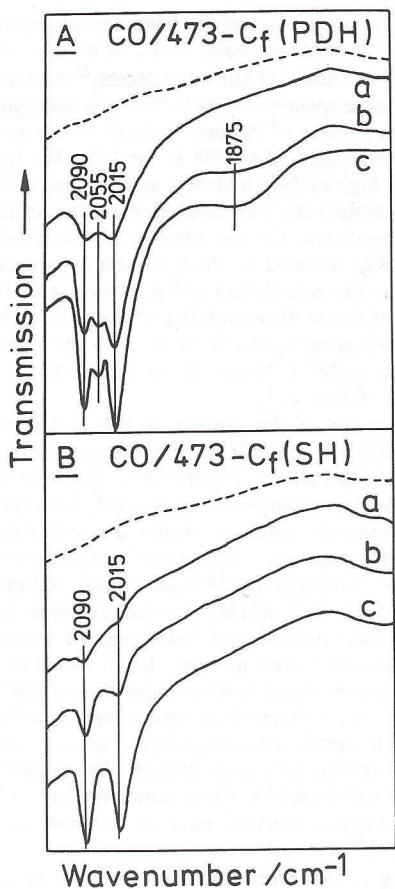
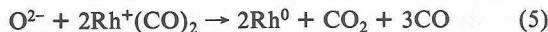


Figure 2. Infrared spectra of CO adsorbed (40 Torr of CO for 20 min) at 298 (a), 373 (b), and 473 K (c) on a HMDS-treated (A) and a water vapor-treated (B) catalyst sample (473-C<sub>f</sub>).

to van't Blik et al.,<sup>28,30,31</sup> the re-formation of Rh<sup>0</sup> at the expense of Rh<sup>+</sup> may take place via the reductive desorption step:



If the elimination of the twin bands characteristic of the geminal species is indeed a result of the occurrence of such a reductive desorption process, the absence of the Rh<sub>x</sub>(CO) species is most probably a consequence of the depletion of the associated CO ligands as a result of their involvement in additional surface reactions activated at the higher temperatures. Adsorbed CO may react to give formate species on the support with the involvement of surface -OH groups,<sup>14</sup> and/or be involved in a Boudouard reaction (2CO → CO<sub>2</sub> + C).<sup>18</sup> The bridging species might be the reactive carbonyls for these reactions. Carbon deposition on Rh metal particles may dilute the active metal sites, thereby contributing to the suppression of the intensity of the Rh<sub>x</sub>(CO) species. These suggestions do not contradict the suggested re-formation of Rh aggregates;<sup>4,28,31</sup> rather, they may explain why their existence has not been detected by infrared spectroscopy.

**CO Adsorption on Partially Dehydroxylated Fresh Catalyst Samples.** The catalyst samples used to obtain the results presented above were relatively strongly hydroxylated, since they had undergone evacuation at only 77 K after H<sub>2</sub> reduction. When evacuation was performed instead at 473 K for 30 min, the degree of surface hydroxylation of sample 473-C<sub>f</sub> was significantly reduced, as shown by the weaker infrared absorption in the O-H stretching region. After HMDS treatment, the surface density of -OH groups was further reduced [sample 473-C<sub>f</sub>(PDH)]. To elucidate further the role of surface -OH groups, another sample of the same catalyst preparation was exposed to 2 Torr of H<sub>2</sub>O vapor at 298 K for 30 min, followed by evacuation at 298 K for

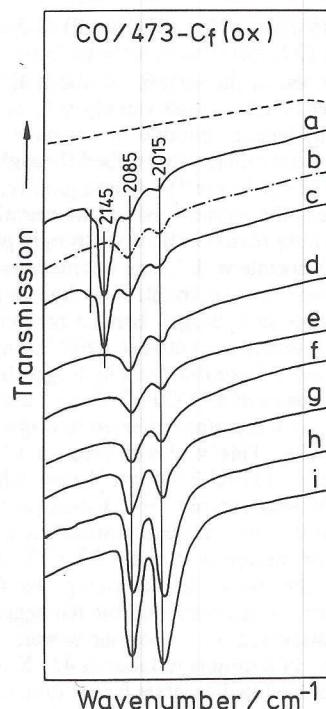


Figure 3. Infrared spectra of CO adsorbed on catalyst sample 473-C<sub>f</sub> treated in a static atmosphere of 100 Torr of dry O<sub>2</sub> at 298 K for 30 min followed by evacuation at the same temperature for 30 min prior to in situ exposure to 40 Torr of CO for 5 min at 77 (a), 100 (c), 180 (d), 230 (e), and 270 K (f), and for 20 min at 298 (g), 373 (h), and 473 K (i). Spectrum b was obtained after evacuation at 77 K for 5 min.

10 min. This sample is designated 473-C<sub>f</sub>(SH), where the SH means strongly hydroxylated.

CO adsorption on the samples 473-C<sub>f</sub>(PDH) and 473-C<sub>f</sub>(SH) at 298–473 K gave rise to the carbonyl spectra shown in parts A and B of Figure 2, respectively. The latter spectra exhibit the twin bands diagnostic of the geminal species, with no indication of linear or bridging species. In contrast, CO adsorption on the 473-C<sub>f</sub>(PDH) sample (Figure 2A) exhibits the absorptions diagnostic of geminal species together with those of the linear and bridging species (bands at 2055 and 1875 cm<sup>-1</sup>, respectively).

These results confirm the role of surface -OH groups in enhancing the oxidative conversion of Rh<sup>0</sup> to Rh<sup>+</sup>. For example, the strongly hydroxylated sample [473-C<sub>f</sub>(SH)] underwent almost complete oxidation of Rh<sup>0</sup> at temperatures (298 K, spectrum a; and 373 K, spectrum b) at which the dissociation of CO is not expected.<sup>7</sup> The sample which had been evacuated at only 77 K (and consequently was still strongly hydroxylated) was oxidized less effectively (cf. spectra h and j in Figure 1A). On the other hand, dehydroxylation (though only partial), produced a surface [473-C<sub>f</sub>(PDH)] on which the oxidative conversion to Rh<sup>+</sup> is much less effective even at a temperature (473 K, spectrum c) at which CO is expected to dissociate.

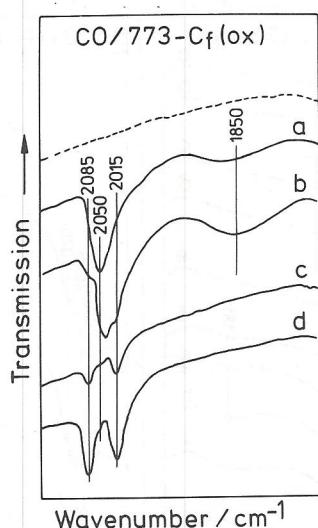
Further, the frequency observed for the bridging carbonyl species formed on 473-C<sub>f</sub>(PDH) upon adsorption of CO at 373 K assumes a value (1875 cm<sup>-1</sup>) much higher than that (1815 cm<sup>-1</sup>) observed (spectrum j, Figure 1A) for the bridging carbonyl species on the hydroxylated sample (473-C<sub>f</sub>) at the same adsorption temperature. This observation is consistent with the presumption stated above regarding a possible retardation of Rh surface mobility in an -OH-rich environment and a consequent retardation of the metal particle growth. The role of surface hydroxyl groups is discussed more fully below.

**CO Adsorption on Oxygen-Treated Fresh Catalyst Samples.** To throw more light on the oxidative conversion of reduced Rh<sup>0</sup>, freshly reduced catalyst samples were treated in a static atmosphere of 100 Torr of dry O<sub>2</sub> at 298 K for 30 min followed by evacuation at the same temperature for 30 min before exposure to CO. These samples are designated 473-C<sub>f</sub>(OX) and 773-C<sub>f</sub>(OX). The infrared spectra obtained after adsorption of CO at

(30) van't Blik, H. F. J. Ph.D. Thesis, Technical University, Eindhoven, The Netherlands, 1984.

(31) van't Blik, H. F. J.; van Zon, J. B. A. D.; Koningsberger, D. C.; Prins, R. J. *Mol. Catal.* 1984, 25, 379.

Fig. 5

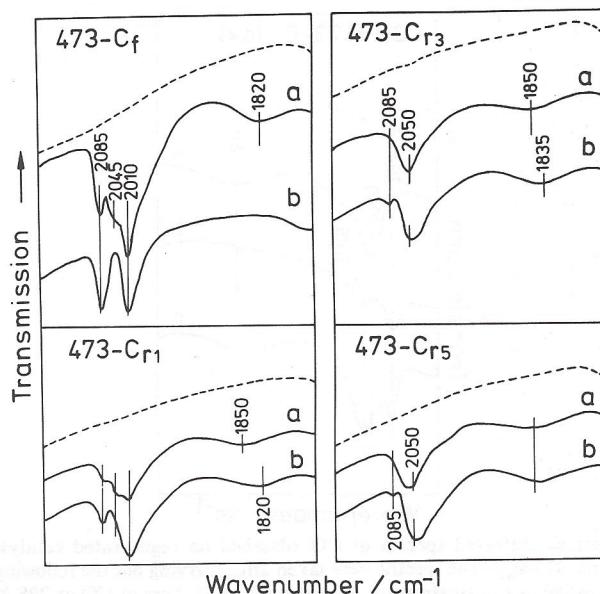


**Figure 4.** Infrared spectra of CO adsorbed on catalyst sample 773-C<sub>f</sub>. The spectra were taken after carrying out the following successive in situ treatments: (a) exposure to 40 Torr of CO at 298 K for 20 min; (b) evacuation followed by exposure to 100 Torr of dry O<sub>2</sub> at 298 K for 30 min and then further evacuation at 298 K for 5 min; (c) increasing the sample temperature to 373 K for 20 min; and (d) reexposure to 40 Torr of CO at 298 K for 20 min.

various temperatures are summarized in Figures 3 and 4, respectively.

Spectrum a in Figure 3 clearly shows the characteristic twin bands (at 2015 and 2085 cm<sup>-1</sup>) at 77 K indicating the existence of Rh<sup>+</sup> on sample 473-C<sub>f</sub>(OX). These two carbonyl bands were the only ones detectable after evacuation at 77 K and removal of the physisorbed CO (spectrum b). Spectra c-i in Figure 3 demonstrate that the intensity of these bands gradually increased with increasing adsorption temperature up to 473 K. These bands are diagnostic of Rh<sup>+(CO)<sub>2</sub></sup>; their resolution, together with the absence of the absorption characteristic of the bridging species at 1760–1920 cm<sup>-1</sup>, excludes the existence of Rh<sup>0</sup> sites at a detectable level. This result indicates that the O<sub>2</sub> treatment at room temperature was sufficient to transform almost all the Rh<sup>0</sup> aggregates into Rh<sup>+</sup> sites under these mild conditions. Further oxidation of Rh to form species in valence state >+1 is less likely. Bands at 2116 and 2136 cm<sup>-1</sup>, which were previously assigned to Rh<sup>2+</sup> and Rh<sup>3+</sup> species, respectively,<sup>32</sup> have not been observed for any of the sample treatments in the present study. Admittedly, however, Rh<sup>3+</sup> species could have escaped detection if Rh<sup>3+</sup> species formed by oxidation in O<sub>2</sub> were reduced back to Rh<sup>+</sup> on admission of CO.<sup>33</sup>

The effect of O<sub>2</sub> on sample 773-C<sub>f</sub>, which originally contained the larger metal particles, is shown by the spectra of Figure 4. The presence of Rh<sup>0</sup> aggregates after CO adsorption at room temperature is evident from spectrum a, which exhibits the bands characteristic of the linear Rh(CO) species (2050 cm<sup>-1</sup>) and the bridging species (1850 cm<sup>-1</sup>). Exposure of the sample to an atmosphere of 100 Torr of O<sub>2</sub> at room temperature after pumping off the CO led to spectrum b of Figure 4, in which two relatively weak shoulders at 2015 and 2085 cm<sup>-1</sup> are present, indicating the formation of some Rh<sup>+</sup> sites. The most intense feature, however, is still the band characteristic of linear Rh(CO) species, now shifted to 2040 cm<sup>-1</sup>. This observation indicates that O<sub>2</sub>-assisted conversion of Rh<sup>0</sup> to Rh<sup>+</sup> slows down markedly when Rh is present as large metal particles. The effect of Rh particle size on the oxidation of the metal by O<sub>2</sub> is well documented.<sup>34</sup> The appearance of the twin bands after CO adsorption seems to be related to the presence of oxygenated species bound to the metal. A similar conclusion was reached by Primet,<sup>1</sup> who observed a band



**Figure 5.** Infrared spectra of CO adsorbed (40 Torr of CO) on the fresh and regenerated catalyst samples at 298 (a) and 473 K (b) for 20 min.

at 2128 cm<sup>-1</sup> attributable to trigonal ORhCO species,<sup>5</sup> but only when the O<sub>2</sub> treatment was carried out at 473 K with a catalyst obtained at reduction temperatures as high as 1273 K.

When the temperature was increased to 373 K for 20 min with the sample exposed to CO, spectrum c of Figure 4 was obtained. This spectrum indicates advanced disintegration and oxidation of the metal particles, as the band for bridging CO species had vanished, with the band at 2050 cm<sup>-1</sup> reduced to a weak shoulder. Readmission of CO at 298 K (spectrum d, Figure 4) led to an enhancement of the twin bands, indicating the predominance of Rh<sup>+(CO)<sub>2</sub></sup> species with only small contributions of Rh(CO) species, indicated by a weak shoulder at 2050 cm<sup>-1</sup>.

These results demonstrate that the larger Rh<sup>+</sup> aggregates can be oxidized to only a limited extent at 298 K (spectrum b, Figure 4), in contrast to the smaller Rh<sup>0</sup> aggregates (spectrum g, Figure 3), and that an effective oxidation was not possible unless the temperature was raised to at least about 373 K (spectrum c, Figure 4). These results suggest the following: (1) the reaction involving oxygen may proceed through a chemisorption on the metal particles, which occurs more rapidly at high temperatures, and (2) the formation of insignificant proportions of Rh<sup>+</sup> on sample 773-C<sub>f</sub> as a result of adsorption of CO at 773 K (cf. spectrum j, Figure 1B) is initiated by a much weaker oxidizing agent than atomic oxygen produced by CO dissociation; in other words, the oxidative role envisaged for surface -OH groups (as stated above) is further substantiated.

**CO Adsorption on Regenerated Catalyst Samples.** CO adsorption in the temperature range 298–473 K on the fresh catalyst sample 473-C<sub>f</sub> and on its regenerated modifications 473-C<sub>r1</sub>, 473-C<sub>r3</sub>, and 473-C<sub>r5</sub> gave rise to the spectra shown in Figure 5. The samples were regenerated by the procedure described under Experimental Methods.

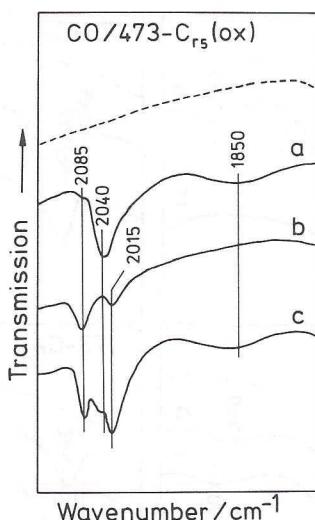
CO adsorption on the fresh catalyst 473-C<sub>f</sub> produced the carbonyl features in the infrared spectrum discussed above. A comparison of spectra for CO adsorption at 298 and 473 K on fresh and regenerated samples is shown in Figure 5. Recall that CO adsorption at 298 K converts a proportion of the highly dispersed Rh<sup>0</sup> to Rh<sup>+</sup>, and at 473 K, when the dissociation of CO can occur, Rh<sup>+</sup> clearly predominates.

On the regenerated sample 473-C<sub>r1</sub>, CO adsorption at 298 K gave rise to the twin bands (spectrum a) indicative of Rh<sup>+(CO)<sub>2</sub></sup> species, which are significantly reduced in intensity relative to those of sample 473-C<sub>f</sub> and to a band indicative of bridging Rh<sub>x</sub>(CO) species; this band is shifted to higher frequency (1850 cm<sup>-1</sup>). At 473 K, however, the twin bands were reinforced again, and the band at 1850 cm<sup>-1</sup> shifted back to its original low frequency (1820 cm<sup>-1</sup>). The twin bands are no longer well resolved, thus enclosing

(32) Rice, C. A.; Worley, S. D.; Curtis, C. U.; Guin, J. A.; Tarrer, A. R. *J. Chem. Phys.* 1981, 74, 6487.

(33) Kellogg, G. L. *Surf. Sci.* 1986, 171, 359.

(34) Vis, J. C.; van't Blik, H. F. J.; Huijzinga, T.; van Grondelle, J.; Prins, R. *J. Catal.* 1985, 95, 333.



**Figure 6.** Infrared spectra of CO adsorbed on regenerated catalyst sample 473-C<sub>r5</sub>. The spectra were taken after carrying out the following successive *in situ* treatments: (a) exposure to 40 Torr of CO at 298 K for 20 min; (b) pumping off of CO followed by exposure to 100 Torr of dry O<sub>2</sub> at 298 K for 30 min and then further evacuation at 298 K for 5 min; and (c) reexposure to 40 Torr of CO at 298 K for 20 min.

an appreciable contribution from the absorption (at 2050 cm<sup>-1</sup>) of the linear Rh(CO) species. These results show that Rh<sup>0</sup> aggregates had been re-formed during this first regeneration. The Rh<sup>0</sup> aggregates thus re-formed could be partially reoxidized upon exposure to a CO atmosphere at 473 K (spectrum b), although to a much lesser extent than on the freshly reduced sample 473-C<sub>r</sub>.

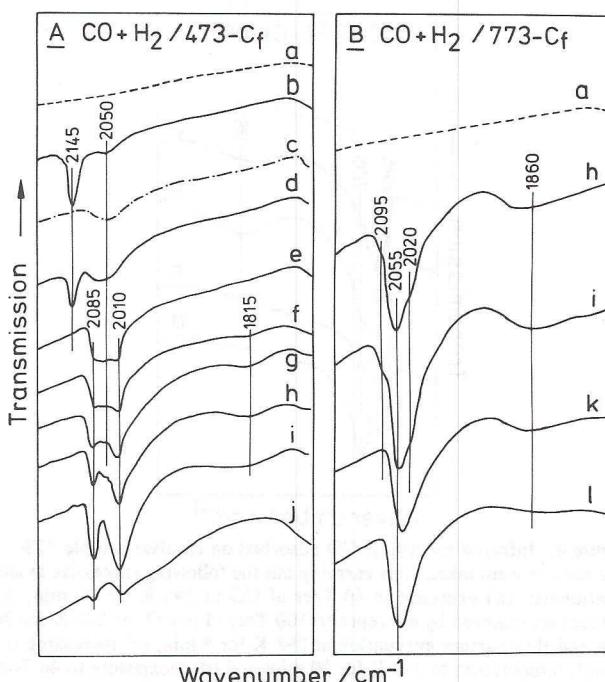
CO adsorption on the triply regenerated sample 473-C<sub>r3</sub> at 298 K led to a spectrum clearly indicating the re-formation of Rh<sup>0</sup> aggregates. These aggregates, however, exhibited a notable resistance to oxidation even at 473 K (spectrum b). After two additional regenerations, sample 473-C<sub>r5</sub> showed only insignificant metal particle disintegration and conversion to Rh<sup>+</sup> upon CO adsorption at 473 K.

These results suggest that successive cycles of CO adsorption and regeneration of a catalyst sample in H<sub>2</sub> causes deterioration of the dispersion and progressive formation of larger Rh<sup>0</sup> aggregates, which then exhibit increased resistance to the oxidative conversion to Rh<sup>+</sup>, even at 473 K.

O<sub>2</sub> treatment of the regenerated sample 473-C<sub>r5</sub> partially restored the dispersion (Figure 6). When sample 473-C<sub>r5</sub> was exposed to 100 Torr of O<sub>2</sub> at 298 K (spectrum b, Figure 6), the absorptions characteristic of the linear and bridging species were eliminated, and well-resolved, but weak, absorptions characteristic of the geminal species developed. When a fresh dose of CO was subsequently admitted at 298 K (spectrum c, Figure 6), the characteristic absorptions of both the linear and bridging species reappeared, and those of the geminal species became more intense. These results demonstrate that for the regenerated sample, complete conversion of the Rh into dispersed Rh<sup>+</sup> sites could not be achieved, even with O<sub>2</sub> treatment, in contrast to the results for the fresh catalyst sample 773-C<sub>f</sub>(OX) (cf. spectrum d, Figure 4). We therefore infer that the extent of Rh<sup>0</sup> aggregation induced by the five successive cycles including regenerations exceeds that produced during the reduction at a high temperature (773 K).

**Influence of H<sub>2</sub> and H<sub>2</sub>O on CO Adsorption on Fresh and Regenerated Catalysts.** The effect of H<sub>2</sub> on the adsorption of CO on the fresh catalyst samples 473-C<sub>f</sub> and 773-C<sub>f</sub> is shown by the carbonyl spectra in parts A and B of Figure 7, respectively. The spectra were obtained after the coadsorption of 40 Torr of a 1:1 (molar) CO + H<sub>2</sub> mixture at various temperatures (77–773 K).

The comparison of the spectra obtained for sample 473-C<sub>f</sub> in the presence (Figure 7A) and absence (Figure 1A) of H<sub>2</sub> shows that there are no significant differences between the two samples in the temperature range 77–373 K. However, when the adsorption was carried out at 473 K (a temperature at which the dissociation and catalytic hydrogenation of CO can occur<sup>14</sup>), a



**Figure 7.** Infrared spectra of CO adsorbed from a gas mixture consisting of 20 Torr of CO and 20 Torr of H<sub>2</sub> on samples 473-C<sub>f</sub> (A) and 773-C<sub>f</sub> (B) for 5 min at 77 (b), 100 (d), 180 (e), 230 (f), 270 (g), and 298 K (h), and for 20 min at 373 (i), 473 (j), 573 (k), and 773 K (l). Also shown are the catalyst background spectrum (a) and the spectrum (c) obtained after evacuating CO at 77 K for 5 min.

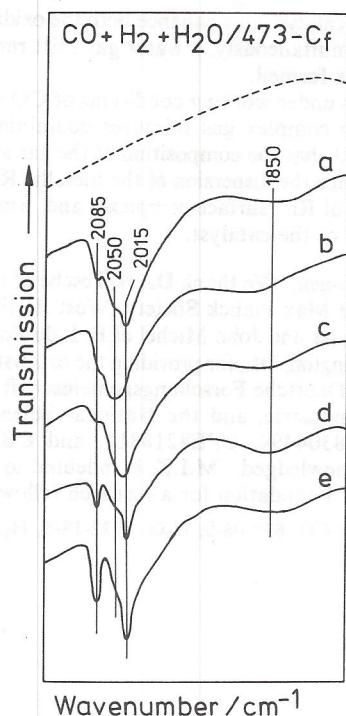
drastic deterioration of the absorptions indicative of the geminal Rh<sup>+</sup>(CO)<sub>2</sub> species occurred when H<sub>2</sub> was present (spectrum j, Figure 7A). These absorptions were eliminated when the time of contact of the adsorbate was increased from 20 to 30 min. In *in situ* infrared measurements reported by Solymosi et al.<sup>14</sup> suggested the importance of the geminal species in the catalytic hydrogenation of CO on Rh/Al<sub>2</sub>O<sub>3</sub> catalysts. Accordingly, the disappearance of the twin bands of the geminal species in the presence of H<sub>2</sub> can well be ascribed to the depletion of the CO ligands as a consequence of their involvement in a surface reaction with H<sub>2</sub>.

For the catalyst sample 773-C<sub>f</sub>, a similar comparison between the spectra given in Figure 7B and the corresponding spectra (obtained in the absence of H<sub>2</sub>) given in Figure 1B shows that even at an adsorption temperature as high as 773 K, the presence of H<sub>2</sub> does not alter the carbonyl bands of the Rh(CO) and Rh<sub>x</sub>(CO), which dominate the spectra in this case. These results complement those obtained for sample 473-C<sub>f</sub> (Figure 7A), confirming the lack of reactivity of the linear and bridging carbonyl species with hydrogen under the present experimental conditions, irrespective of the temperature regime up to 773 K.

The above results suggest the inference that the presence of H<sub>2</sub> hinders further oxidation of dispersed or aggregated Rh<sup>0</sup> to Rh<sup>+</sup> by attacking the activated CO species involved. Moreover, the results exclude with certainty the occurrence of CO dissociation at temperatures  $\leq$  298 K and, hence, the contribution of CO to the oxidative formation of Rh<sup>+</sup> observed in that temperature range, thus confining this role to surface -OH groups; otherwise, the carbonyl spectra obtained at temperatures  $\leq$  298 K (Figure 7A) should have lacked the characteristic bands of the geminal species.

The addition of water vapor at 2 Torr to the CO + H<sub>2</sub> gas mixture (used above) in contact with catalyst sample 473-C<sub>f</sub> at 298 K led to some changes in the structure of the composite absorption centered around 2050 cm<sup>-1</sup>, as shown by the comparison between spectra a and b in Figure 8. It is clear that these changes are mainly the result of a weakening of the absorptions at 2015 and 2085 cm<sup>-1</sup>, which indicates a decrease of the surface concentration of the Rh<sup>+</sup>(CO)<sub>2</sub> species.

When this water-containing mixture of CO + H<sub>2</sub> was replaced by an atmosphere of pure water vapor at 2 Torr, spectrum d of Figure 8 was obtained. This spectrum shows a reinforcement of



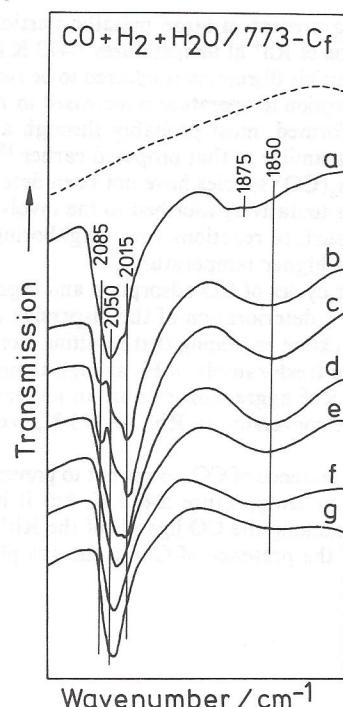
**Figure 8.** Infrared spectra of CO adsorbed on catalyst sample 473-C<sub>f</sub>. The spectra were taken after carrying out the following successive *in situ* treatments: (a) exposure to a gas mixture consisting of 20 Torr of CO and 20 Torr of H<sub>2</sub> at 298 K for 20 min; (b) admission of 2 Torr of water vapor to the gas phase of (a) at 298 K for 20 min; (c) pumping off of the gas phase of (b) at 298 K for 5 min; (d) exposure to 2 Torr of water vapor at 298 K for 20 min; and (e) pumping off of the water vapor followed by reexposure to a mixture of 20 Torr of CO and 20 Torr of H<sub>2</sub> at 298 K for 20 min.

the absorptions of the geminal species at the expense of the linear species (indicated by the band at 2050 cm<sup>-1</sup>). This spectral modification was further enhanced when the H<sub>2</sub>O vapor was pumped off and the CO + H<sub>2</sub> mixture readmitted at 298 K, as shown by spectrum e of Figure 8.

We emphasize two facts demonstrated by these results: (1) in the presence of the CO + H<sub>2</sub> atmosphere, water reduces the surface concentration of the Rh<sup>+</sup>(CO)<sub>2</sub> species; but (2) in the absence of CO and H<sub>2</sub>, water enhances the formation of these geminal species at the expense of the linear ones. The former experimental result can be understood as a consequence of a decrease in the surface coverage by CO rather than of a reduced density of Rh<sup>+</sup> sites available. The second possibility would mean that water assists a reductive conversion of Rh<sup>+</sup> to Rh<sup>0</sup>, which would contradict the established results, including those of the present investigation. The decrease in the surface coverage by CO could be a result of the involvement of Rh<sup>+</sup>(CO)<sub>2</sub> species in a reaction with water, most probably the water gas shift reaction; such a reaction is expected<sup>28,30,31</sup> to occur on Rh/Al<sub>2</sub>O<sub>3</sub> at temperatures lower than that required for the catalytic hydrogenation of CO (i.e., temperatures <473 K).

The second experimental fact is compatible with the role assumed for surface hydroxyl groups in the oxidative conversion of Rh<sup>0</sup> to Rh<sup>+</sup> in the absence of CO in the gas phase, in accordance with the results obtained for the 473-C<sub>f</sub>(SH) sample (Figure 2B). The readmission of CO after pumping off of the water vapor would then lead to carbonylation and infrared detection of Rh<sup>+</sup> sites that arose.

To determine the effect of the adsorption temperature (298–773 K) on the coadsorption of CO, H<sub>2</sub>, and water, experiments were done with sample 773-C<sub>f</sub>; the spectra are shown in Figure 9. The admission of 2 Torr of water to the sample after exposure to CO + H<sub>2</sub> at 298 K for 20 min led to spectrum b, which has a band structure different from that shown in spectrum a, obtained with CO + H<sub>2</sub> in the absence of water. The absorptions due to the Rh<sup>+</sup>(CO)<sub>2</sub> species (at 2015 and 2085 cm<sup>-1</sup>) are enhanced, and



**Figure 9.** Infrared spectra of CO adsorbed on sample 773-C<sub>f</sub>. The spectra were taken after carrying out the following successive *in situ* treatments: (a) exposure to a gas mixture consisting of 20 Torr of CO and 20 Torr of H<sub>2</sub> at 298 K for 20 min; (b) admission of 2 Torr of water vapor to the gas mixture of (a) at 298 K for 20 min; and (c) increasing the adsorption temperature to 373 followed by 473 (d), 573 (e), 673 (f), and 773 K (g) for 20 min.

the center of the band indicative of the Rh<sub>x</sub>(CO) species is shifted from 1875 to 1850 cm<sup>-1</sup>. These changes in the spectrum associated with the presence of water indicate an enhanced oxidative formation of Rh<sup>+</sup> sites and disintegration of Rh<sup>0</sup> aggregates, respectively. This behavior is contrasted to that of sample 473-C<sub>f</sub> (Figure 8). These trends were still observed at 373 K (spectrum c, Figure 9). However, when the adsorption temperature was increased to 473 K (spectrum d) and higher (spectra e–g) (temperatures at which CO activation can occur), the Rh<sup>+</sup>(CO)<sub>2</sub> species were no longer detectable. These spectra (in particular, f and g) reveal the persistence of the linear species and, to a lesser extent, the bridging species.

The above results may imply that water in the presence of CO enhances both the Rh<sup>0</sup> → Rh<sup>+</sup> conversion and, simultaneously, reaction with the Rh<sup>+</sup>(CO)<sub>2</sub> species thus formed; whenever the Rh<sup>+</sup>(CO)<sub>2</sub> species are abundant, the latter reaction predominates. Alternatively, the results may mean that the Rh<sup>+</sup>(CO)<sub>2</sub> species have become unstable and are no longer able to provide a spectrum diagnostic of the Rh<sup>0</sup> → Rh<sup>+</sup> reaction. These two possibilities are closely related, and neither can be excluded.

### Conclusions

- Heating Rh(NO<sub>3</sub>)<sub>3</sub>-impregnated γ-Al<sub>2</sub>O<sub>3</sub> in H<sub>2</sub> at a low temperature (473 K) for 1 h results in an almost complete reduction of the rhodium into highly dispersed metallic Rh<sup>0</sup>. CO adsorption at a temperature as low as 100 K initiates a partial conversion of the Rh<sup>0</sup> to Rh<sup>+</sup> ions. The present investigation has added evidence of a disruptive oxidation process assisted by CO; the oxidizing agent is suggested to be surface -OH groups.<sup>6</sup> At a higher adsorption temperature (230 K), unoxidized Rh<sup>0</sup> commences to aggregate via surface diffusion, a process that is critically controlled by the degree of surface hydroxylation. At a still higher CO adsorption temperature (473 K), the oxidation to Rh<sup>+</sup> is more rapid, the occurrence of another mechanism in which atomic oxygen produced by dissociative chemisorption of CO is inferred to play a role.

- When the reductive preparation of the catalyst is carried out at a higher temperature (773 K), the Rh<sup>0</sup> produced is poorly

dispersed, being present in large metallic particles. The CO-assisted formation of  $\text{Rh}^+$  at temperatures  $<473\text{ K}$  is then strongly retarded;  $\text{Rh}^0$  particle disruption is inferred to be rate determining. As the CO adsorption temperature is increased to 773 K, particles of  $\text{Rh}^0$  are re-formed, most probably through a reductive desorption process similar to that proposed earlier.<sup>18</sup> Surprisingly, the relevant  $\text{Rh}_x(\text{CO})$  species have not been detected; their low concentration is tentatively ascribed to the involvement of their CO ligands in surface reactions with neighboring  $-\text{OH}$  groups activated at the higher temperatures.

3. Successive cycles of CO adsorption and regeneration in  $\text{H}_2$  at 473 K cause a deterioration of the dispersion of the metallic precursor to an extent exceeding that resulting from the reductive preparation of a fresh sample in  $\text{H}_2$  at high temperatures. The resulting large  $\text{Rh}^0$  aggregates exhibit an increasing resistance to the oxidative conversion to  $\text{Rh}^+$  at 473 K, even in an  $\text{O}_2$  atmosphere.

4.  $\text{H}_2$ , in the presence of CO, seems not to prevent the oxidation of  $\text{Rh}^0$  to  $\text{Rh}^+$  at temperature  $\leq 473\text{ K}$ , but it hinders further oxidation by attacking the CO ligands of the  $\text{Rh}^+(\text{CO})_2$  species.

5. Water in the presence of CO in the gas phase in contact

with a reduced catalyst may enhance both the oxidative formation of  $\text{Rh}^+$  and, simultaneously, a water gas shift reaction with the  $\text{Rh}^+(\text{CO})_2$  thus formed.

6. Catalysts under working conditions of  $\text{CO} + \text{H}_2$  reactions are exposed to complex gas mixtures containing water. We therefore expect that the composition of the gas atmosphere will strongly influence the dispersion of the metallic Rh particles and the abundance of  $\text{Rh}^+$  surface complexes and, hence, the activity and selectivity of the catalyst.

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*Registry No.* CO, 630-08-0;  $\text{H}_2\text{O}$ , 7732-18-5;  $\text{H}_2$ , 1333-74-0; Rh, 7440-16-6.