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FTIR study of the rearrangement of adsorbed CO species on Al_2O_3-supported rhodium catalysts

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The adsorption of CO at low temperatures (130–293 K) has been investigated on Rh/Al_2O_3 catalysts of low (0.001–1 wt%) Rh loadings by means of Fourier transform infrared spectroscopy. The surface structure of Rh produced at different reduction temperatures (573 and 1173 K) was shock-cooled to 130 K, where the addition of CO caused the appearance of the band due to bridge-bonded CO ($(Rh^0)_2$–CO) on all samples. The appearance of the bands due to gem-dicarbonyl ($Rh^+(CO)_2$) and linearly bonded CO (Rh_x–CO) depended on the Rh content and the reduction temperature of the catalysts. The positions and the integrated absorbances of the symmetric and asymmetric stretchings of the $Rh^+(CO)_2$ changed with temperature. On the basis of the above findings the rearrangement of the adsorbed CO species (indirectly that of surface Rh) is discussed.

Keywords: low-temperature CO adsorption, small Rh loadings on alumina, rearrangement of CO surface species, FTIR spectroscopy

1. Introduction

The interaction between CO and supported Rh was the subject of numerous papers in the last decade. With respect to adsorption of CO on differently pretreated Rh/Al_2O_3 catalysts (at 300 K and at higher temperature) several CO adsorbed species have been established by IR spectroscopy. It was found that, when the reduction temperature of the Rh/Al_2O_3 sample was 573 K (or lower), the gem-dicarbonyl species ($Rh^+(CO)_2$) immediately formed on the admission of CO. This was interpreted by the oxidative disruption of Rh_x crystallites with the help of surface OH groups on the supporting oxides [1–12]. On the Rh/Al_2O_3 samples reduced at higher (673–1173 K) temperatures the oxidative disruption was much slower, as in the adsorption of CO at 300 K the dominant bands were due to linearly adsorbed (2040–2065 cm^{-1}) and bridge-bonded CO (1850 cm^{-1}) on these samples, and IR bands due to gem-dicarbonyl (2100 and 2035 cm^{-1}) appeared only after a long induction time, and the rate of their formation was very low [1–4].

An interesting feature of the interaction of CO with Rh/Al_2O_3 ($T_R = 573$ K or lower) is that above 448 K CO reduces Rh^+ to Rh^0 and promotes its agglomeration to Rh_x [3,4,7]. This was indicated in the infrared spectrum by the gradual attenuation of the bands due to gem-dicarbonyl species with the simultaneous development of the IR features due to the Rh_x–CO species [3,4].

The data published so far for the above phenomena refer to relatively high (0.5–5%) Rh loadings on oxide catalysts. The decrease of noble metal loadings in the practical catalysts is highly requested due to their high price. In this work we present FTIR results obtained on Al_2O_3-supported Rh of 0.001–1%. Our primary aim was to get information on the interaction of CO with highly dispersed alumina-supported Rh catalysts. We expected that these data would be helpful for a better understanding of the mechanism of the above interaction. Special attention was devoted to the formation of bridge-bonded CO and to the dynamical character of gem-dicarbonyl formation. To eliminate the falsifying effect of the quick oxidative disruption, the adsorption of CO was investigated at low temperature. The data, on the other hand, would be useful in characterization of the surface structure of the metals formed on low metal loaded catalysts.

2. Experimental

Rh/Al_2O_3 samples were prepared by incipient wetting of γ-alumina (Degussa) with an aqueous solution of $RhCl_3{\cdot}3H_2O$ (Johnson-Matthey). The Rh content varied between 0.001 and 1 wt%. For preparation triply distilled water was used. After impregnation, the samples were dried in air at 373 K and then pressed into self-supporting wafers (30×10 mm, 10 mg/cm^2). The pretreatment of samples was performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 573 K under continuous evacuation; (b) oxidized with 13.3 kPa O_2 for 30 min at this temperature; (c) evacuated for 30 min at 573 K; and (d) reduced in circulating H_2 (13.3 kPa) for 60 min at 573 and 1173 K, respectively. During reduction the eventually formed water was continuously trapped by a cold finger. This was followed by degassing for 30 min and by cooling the sample to 133 K. The gases used in this study were of high purity (Linde) products.

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Infrared spectra were recorded with a FTS-7 Fourier transform IR spectrometer (Bio-Rad) with a wavenumber accuracy of ± 1 cm^{-1}. Typically 16 scans were recorded. All the spectra presented in this work are difference spectra. The spectrum of pretreated catalyst (without CO) taken at 133 K was subtracted from the actual spectrum. Before determining the integral absorbance of the bands, the spectrum of gaseous CO was subtracted from the spectra. Subtractions were made without using a scaling factor ($f = 1.0000$).

3. Results

3.1. CO adsorbed on Rh

Among the bands above 2100 cm^{-1}, which appeared upon low-temperature CO adsorption on Rh/Al_2O_3, the band at 2190 cm^{-1} is assigned to CO strongly physisorbed on Al^{3+}, the 2154 cm^{-1} band is attributed to H-bonded CO [7,9,13] and the 2120 cm^{-1} band can be due to vibration of gas-phase CO. As these bands belong to CO interacting with alumina, they are out of scope for further discussion.

In figure 1 some selected spectra are plotted, which were obtained on different Rh/Al_2O_3 catalysts. The temperature displayed on the spectra shows the lowest temperature at which the spectra first exhibited spectral features due to CO species on Rh.

The spectra of the least Rh-containing (0.001–0.01% Rh) samples reduced at 573 K showed only a very weak band at 1810 cm^{-1} due to the bridge-bonded CO on Rh. Its appearance depended on the Rh content of the catalysts: it could be detected at 183 K on 0.001% Rh/Al_2O_3, at 173 K on 0.005% Rh/Al_2O_3 and at 153 K on 0.01% Rh/Al_2O_3. Its position also depended on the Rh content: it appeared at 1848 cm^{-1} on 1% Rh/Al_2O_3. The spectra of 0.05–1% Rh/Al_2O_3 samples exhibited the gem-dicarbonyl ($Rh^+(CO)_2$) bands at 2100 and 2033 cm^{-1} already at the lowest temperature (133 K) applied in this study.

The increase of the reduction temperature to 1173 K lowered the temperature at which the bands due to bridge-

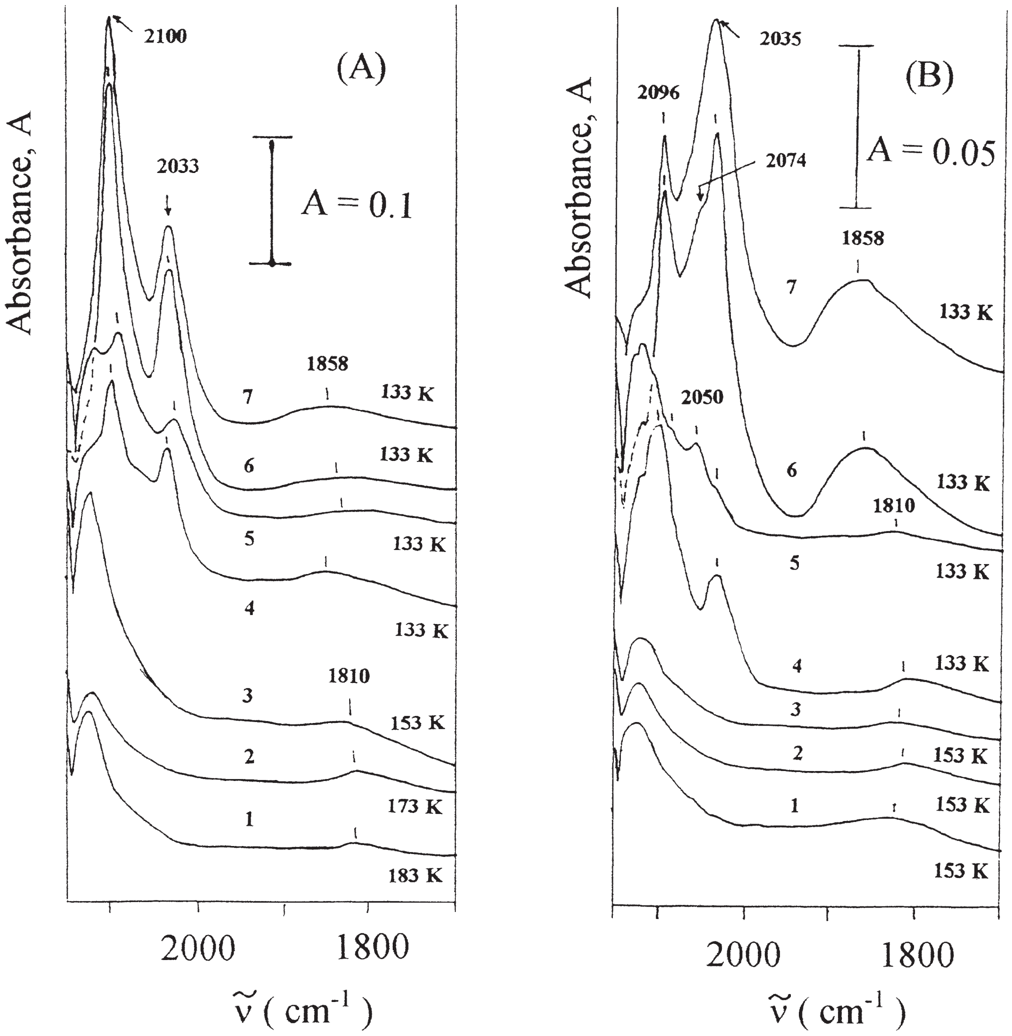

Figure 1. Infrared spectra of Rh/Al_2O_3 catalysts reduced at 573 K (A) and at 1173 K (B) in the presence of 10 Torr CO: 1 – 0.001% Rh/Al_2O_3; 2 – 0.005% Rh/Al_2O_3; 3 – 0.01% Rh/Al_2O_3; 4 – 0.05% Rh/Al_2O_3; 5 – 0.1% Rh/Al_2O_3; 6 – 0.5% Rh/Al_2O_3 and 7 – 1% Rh/Al_2O_3.

Table 1
Temperature of the appearance of CO bands in 10 Torr CO.

Catalyst	Bridged	Gem-dicarbonyl	Linear
$T_R = 573$ K			
0.001% Rh/Al_2O_3	183 K	–	–
0.005% Rh/Al_2O_3	173 K	243 K	–
0.01% Rh/Al_2O_3	153 K	233 K	–
0.05% Rh/Al_2O_3	133 K	133 K	–
0.1% Rh/Al_2O_3	133 K	133 K	–
0.5% Rh/Al_2O_3	133 K	133 K	133 K (sh)
1% Rh/Al_2O_3	133 K	133 K	133 K (sh)
$T_R = 1173$ K			
0.001% Rh/Al_2O_3	153 K	–	–
0.005% Rh/Al_2O_3	153 K	233 K	223 K
0.01% Rh/Al_2O_3	153 K	213 K	133 K
0.05% Rh/Al_2O_3	133 K	133 K	133 K
0.1% Rh/Al_2O_3	133 K	133 K	133 K
0.5% Rh/Al_2O_3	133 K	133 K	133 K
1% Rh/Al_2O_3	133 K	133 K	133 K

bonded CO on Rh appeared (figure 1(B)). The 1810 cm^{-1} band could be detected already at 153 K on the samples of the lowest Rh content. The position of this band shifted to higher wavenumbers with the increase of the Rh content of the samples: it was detected at 1858 cm^{-1} on 0.5 and 1% Rh/Al_2O_3. The other effect of the higher reduction temperature manifested itself in the appearance of the band due to Rh_x–CO species: it could be detected at 2050 cm^{-1} on 0.1% Rh/Al_2O_3 at 133 K, and it appeared at 2074 cm^{-1} on 0.5–1% Rh/Al_2O_3 at 133 K. The bands due to gem-dicarbonyl were registered first at 133 K on the spectra of 0.05–1% Rh/Al_2O_3.

Heating of the 0.001–0.01% Rh/Al_2O_3 samples in CO atmosphere caused the appearance of the gem-dicarbonyl ($T_R = 573$ K) and that of the gem-dicarbonyl and linear CO bands ($T_R = 1173$ K). The data collected in table 1 show that the appearance of the gem-dicarbonyl and linear CO bands depended on the Rh content of the catalysts and on the reduction temperature. On catalysts having 0.05% Rh or more, all characteristic bands appeared at the lowest temperature (133 K) applied.

3.2. Changes of spectral features due to gem-dicarbonyl species

We have determined the exact band positions for the gem-dicarbonyl vibrations during heating of the samples in CO atmosphere. Surprisingly, a monotonous decrease was observed in the positions of both the symmetric and asymmetric stretchings of $Rh^+(CO)_2$.

In figure 2 we plotted the data obtained on 1% Rh/Al_2O_3. We note, however, that the same features were observed with all samples. The position of the symmetric stretching band (2100 cm^{-1} for $T_R = 573$ K and 2096 cm^{-1} for $T_R = 1173$ K) was practically constant between 133 and 193 K, and then it shifted continuously with the increase of the temperature to lower wavenumbers. At 293 K it was detected at 2093 cm^{-1} ($T_R = 573$ K) and at 2087 cm^{-1} ($T_R = 1173$ K) (figure 2(A)). Similar characteristics were monitored for the asymmetric stretching band of $Rh^+(CO)_2$: on the sample reduced at 573 K it shifted monotonously from 2033 cm^{-1} (133 K) to 2025 cm^{-1} (293 K), and on the $T_R = 1173$ K sample from 2035 cm^{-1} (133 K) to 2022 cm^{-1} (293 K) (figure 2(B)).

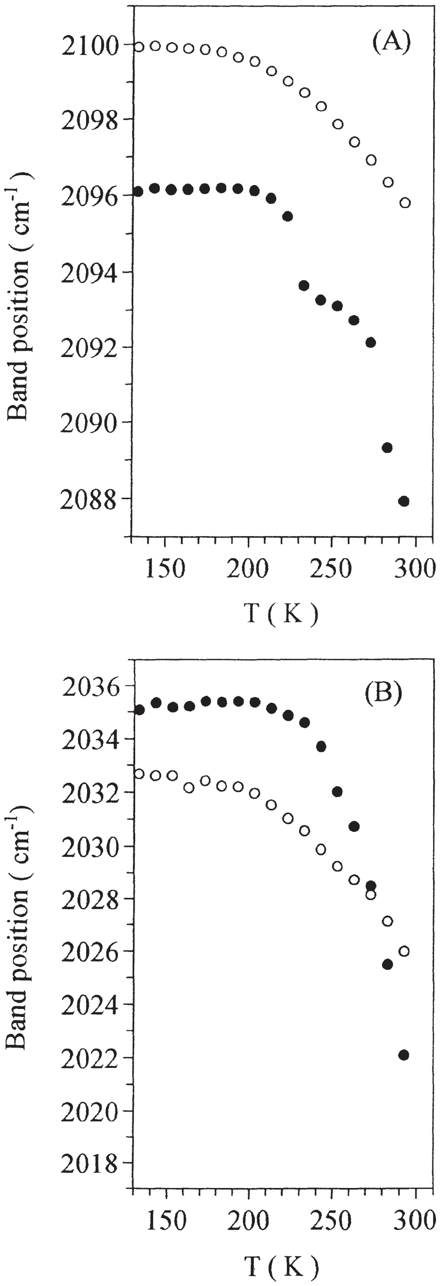

Figure 2. Band positions of the symmetric (A) and asymmetric (B) stretchings of $Rh^+(CO)_2$ on 1% Rh/Al_2O_3 in the presence of 10 Torr CO as the function of the temperature: (○) sample reduced at 573 K and (●) sample reduced at 1173 K.

Besides the shifts in the band positions, we have observed continuous changes in the integrated absorbances of the gem-dicarbonyl bands as an effect of heating in CO atmosphere. The data determined for 1% Rh/Al_2O_3 reduced at 573 and 1173 K are shown in figure 3. The integrated absorbances of both the symmetric and asymmetric vibration bands of $Rh^+(CO)_2$ species were constant up to 173 K, above this temperature they showed a continuous increase with the rise of the temperature on the $T_R = 573$ K sample (figure 3(A)). At the highest temperature applied (293 K) their ratio approached unity, as it was usually found in previous studies at 300 K [1–14].

On the 1% Rh/Al_2O_3 sample ($T_R = 1173$ K) the integrated absorbances of both vibration bands were constant up to 233 K, at higher temperature a slight continuous increase was monitored for both vibrations (figure 3(B)). We note that on this sample the integrated absorbance of the asymmetric band was higher than that of the symmetric one. Their relation was opposite for the sample of $T_R = 573$ K. Another interesting finding is that the ratio of the two integrated absorbances did not approach to the usual value of unity on 1% Rh/Al_2O_3 ($T_R = 1173$ K). In figure 3(B) we also plotted the integrated absorbance of the band indicating the linearly adsorbed CO (2084–2058 cm^{-1}). Its intensity was very low between 133 and 173 K, thus the determination was uncertain at these temperatures. Above 243 K, an appreciable increase in integrated absorbance was experienced, and it shifted to 2058 cm^{-1} with the rise of the temperature.

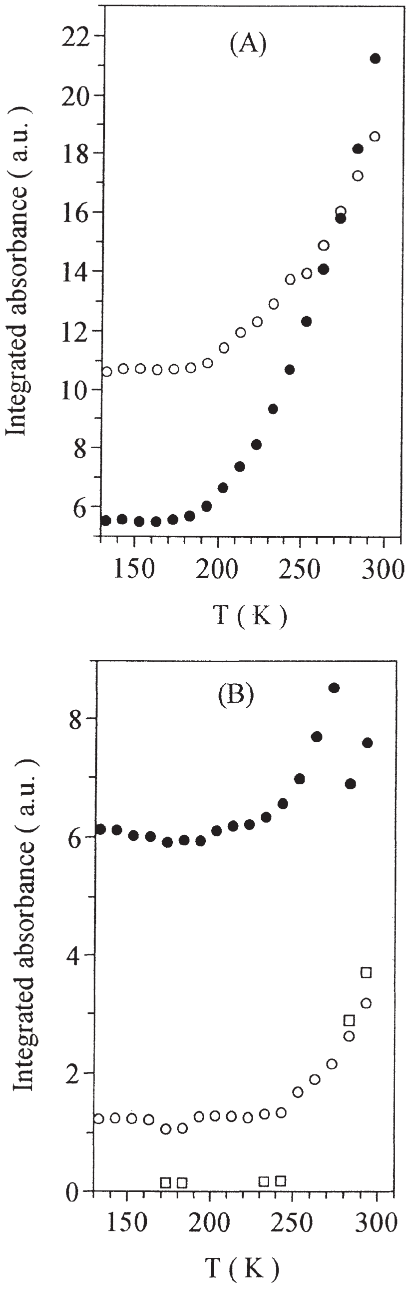

Figure 3. Integrated absorbances of the bands due to adsorbed CO on 1% Rh/Al_2O_3 reduced at 573 K (A) and at 1173 K (B) in 10 Torr CO as the function of the temperature: (○) symmetric stretching of $Rh^+(CO)_2$; (●) asymmetric stretching of $Rh^+(CO)_2$ and (□) linearly bonded CO.

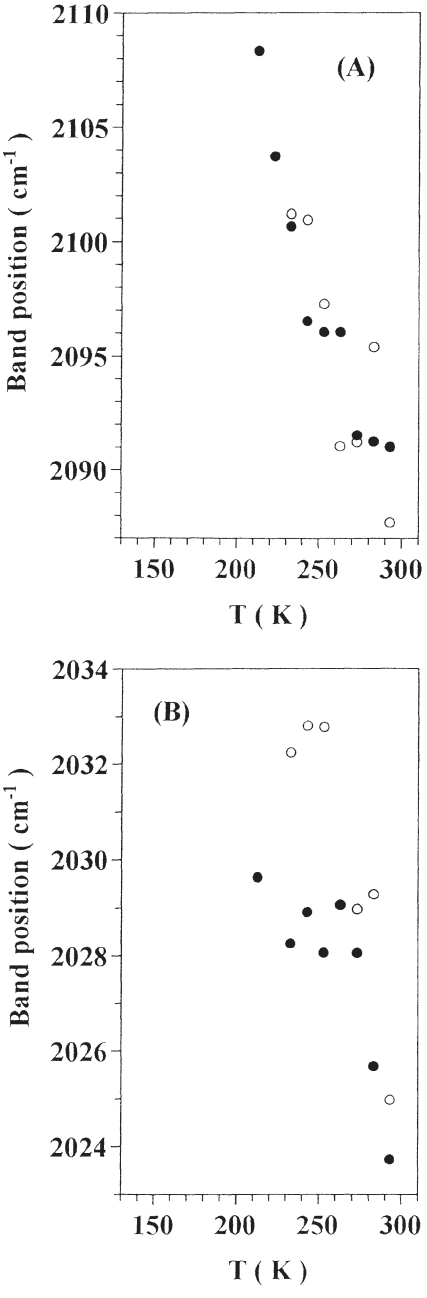

Figure 4. Band positions of the symmetric (A) and asymmetric (B) stretchings of $Rh^+(CO)_2$ on 0.01% Rh/Al_2O_3 in the presence of 10 Torr CO as the function of the temperature: (○) sample reduced at 573 K and (●) sample reduced at 1173 K.

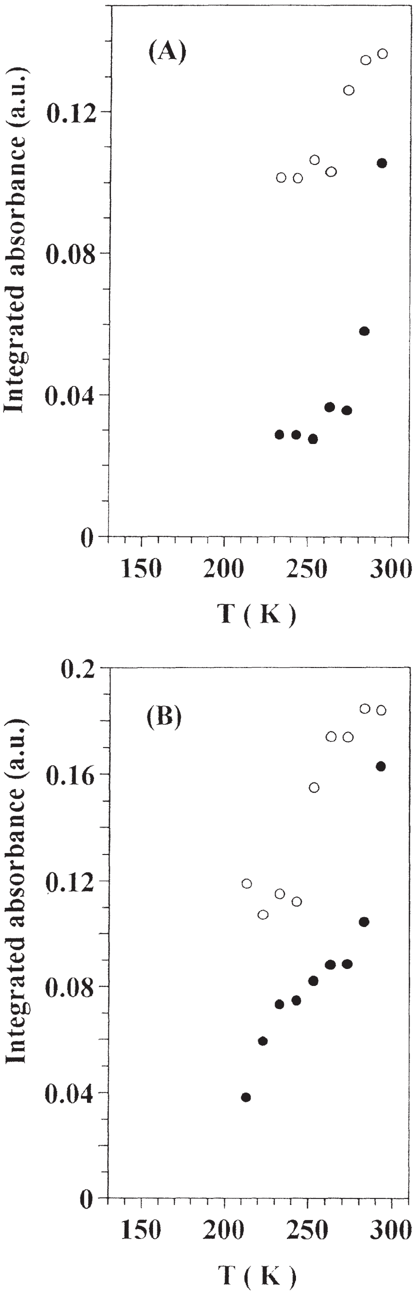

Figure 5. Integrated absorbances of the bands due to adsorbed CO on 0.01% Rh/Al_2O_3 reduced at 573 K (A) and at 1173 K (B) in 10 Torr CO as the function of the temperature: (○) symmetric stretching of $Rh^+(CO)_2$ and (●) asymmetric stretching of $Rh^+(CO)_2$.

The same tendency of the band positions and the integrated absorbances was observed on other Rh/Al_2O_3 catalysts. As an example for this, data obtained on 0.01% Rh/Al_2O_3 catalysts are presented in figures 4 and 5.

4. Discussion

4.1. Formation of CO species adsorbed on Rh

The most striking information of this study is the priority in the appearance of the band due to bridge-bonded CO on alumina-supported Rh with low Rh content. At low temperatures only this band was observed on the 0.001–0.1% Rh/Al_2O_3 samples (table 1), the bands of gem-dicarbonyl CO and the linearly bonded CO (if any) appeared at higher temperatures. Among the bands due to adsorbed CO on Rh, the band characteristic of the bridge-bonded CO appears at the lowest wavenumbers (1858–1810 cm^{-1}), consequently the metal–C bond should be the strongest in this form. Taking this into account, it can be postulated that the formation of bridge-bonded CO is the thermodynamically most favored among the possible forms of adsorbed CO species.

For the formation of bridge-bonded CO some (at least two) adjacent Rh^0 atoms are necessary. We have detected the band at 1810 cm^{-1} first at 183 K on 0.001% Rh/Al_2O_3 ($T_R = 573$ K). Its absence at 133–183 K shows that at these temperatures the surface Rh sites needed for the formation of $(Rh^0)_2$–CO are not yet available. It can be stated that Rh^0 atoms formed during the reduction at 573 K are localized on the alumina surface relatively far apart from each other due to the low Rh content. This state of Rh^0 atoms is conserved by shock-cooling of the sample from the reduction temperature to 133 K. Appreciable surface migration of Rh^0 atoms needs higher temperature to occur. With the rise of the temperature the surface diffusion of Rh^0 atoms leads to the formation of two-dimensional Rh islands with favorable constellation for $(Rh^0)_2$–CO species. Thus CO adsorption may fix the agglomerated Rh^0 atoms by the formation of thermodynamically favored bridge-bonded CO surface species.

Both the increase of the Rh content and the rise of the reduction temperature can enhance the possibility of the formation of two-dimensional Rh islands already during the pretreatment. Accordingly, the $(Rh^0)_2$–CO species could be detected on these samples at lower temperatures (table 1).

In the two-dimensional Rh islands of sufficiently large size (at least 5–7 Rh^0 atoms), some of the Rh^0 atoms would behave as partially positively charged $Rh^{\delta+}$ due to the electronic interaction between agglomerated Rh^0 atoms and the support [15]. The presence of $Rh^{\delta+}$ in Rh islands is detected by the development of IR bands due to gem-dicarbonyl. The higher probability for the formation of Rh islands of this type (and accordingly that for the detection of gem-dicarbonyl) would be the result of either the enhancement of surface diffusion of Rh^0 occurring at higher temperatures (see the results on 0.005–0.01% Rh/Al_2O_3), or that of the increase of Rh content and the rise of the reduction temperature.

The increase of the Rh content and the rise of the reduction temperature, on the other hand, result in the formation of Rh_x crystallites on the surface. In these three-dimensional Rh crystallites, there are Rh^0 atoms surrounded only by Rh^0 atoms. The presence of these Rh^0 atoms with metallic character was documented by the IR band due to linearly (on-top) bonded CO. This band (as a shoulder at 133–273 K) was observed only on 0.5 and 1% Rh/Al_2O_3

among the samples reduced at 573 K and on the catalysts reduced at 1173 K having 0.005% or more Rh.

4.2. Changes of spectral features due to $Rh^+(CO)_2$

From the results obtained on the samples reduced at 573 K it turned out that the spectral features are relatively constant between 133 and 223 K. Concerning the characteristics of $Rh^+(CO)_2$ species (where they were detected), we can state that in this temperature range:

- the bands due to gem-dicarbonyl appeared at the same wavenumbers;
- the integrated absorbances of these bands were constant;
- the ratio of the integrated absorbances ($A_{\mathrm{asym}}/A_{\mathrm{sym}}$) was constant.

Above this temperature range, these features were changed:

- the positions of the bands shifted to lower wavenumbers;
- the integrated absorbances increased;
- the ratio of $A_{\mathrm{asym}}/A_{\mathrm{sym}}$ changed.

These changes occurred at higher temperatures (243–253 K) on the samples reduced at 1173 K.

Formerly, the appearance of the IR bands due to gem-dicarbonyl was exclusively interpreted as a result of the oxidative disruption of three-dimensional Rh_x crystallites [1–13]. Note, however, that in the present experiments we observed gem-dicarbonyl even in those cases where no sign of linearly bonded CO on three-dimensional Rh_x crystallites appeared in the spectra. Another interesting finding is that the integrated absorbance of the band of linearly bonded CO started to increase at the same temperature at which the increase of the integrated absorbances of gem-dicarbonyl bands started (figure 4(B)). If the oxidative disruption was operative in the present case, a decrease of the integrated absorbance for linearly bonded CO should have occurred.

We think that the increase in integrated absorbances of gem-dicarbonyl bands is indicative of the formation of larger two-dimensional Rh agglomerates in the case of Rh/Al_2O_3 samples which contain smaller amounts of Rh and were reduced at 573 K. In this sense the gem-dicarbonyl is characteristic of the agglomeration of Rh^0 into larger two-dimensional Rh islands.

On the samples having more Rh and/or reduced at 1173 K (i.e., three-dimensional Rh_x crystallites exist on their surfaces), the detection of gem-dicarbonyl bands is indicative of disruption of Rh_x crystallites into two-dimensional Rh islands.

5. Conclusions

(i) The most favorable surface species during the low-temperature CO adsorption on alumina-supported Rh with small Rh contents is the bridge-bonded CO.

(ii) The appearance of the bands due to gem-dicarbonyl and linearly bonded CO depends on the Rh content and the reduction temperature of the catalysts.

(iii) The formation of bridge-bonded CO is one of the prerequisites of the formation of gem-dicarbonyl species.

(iv) From the changes of the band positions and the integrated absorbances of the symmetric and asymmetric stretchings of the gem-dicarbonyl it is concluded that CO causes a surface rearrangement of adsorbed CO species, and, consequently, that of surface Rh sites even at low temperature.

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