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Analysis of the IR-Spectral Behavior of Adsorbed CO Formed in $H_2 + CO_2$ Surface Interaction over Supported Rhodium

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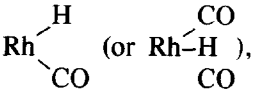
The interaction of hydrogen and carbon dioxide has been investigated by means of infrared spectroscopy on alumina-supported Rh of different crystallite sizes produced by reduction at 573–1173 K with a view to explaining the infrared spectrum of the adsorbed CO produced which is basically different from that observed following CO adsorption on the same samples. It appeared that the adsorbed CO formed on CO_2 or $H_2 + CO_2$ adsorption did not lead to the formation of *gem*-dicarbonyl, i.e., to disruption of the Rh–Rh bond. This behavior is attributed to the presence of adsorbed hydrogen and to the formation of Rh carbonyl hydride, which prevents the disruptive effect of adsorbed CO.

INTRODUCTION

The characteristics of the Rh–CO systems have been the subject of extensive research in the past decade. A special case of this system is that which occurs when the adsorbed CO is produced by a surface reaction and not by the adsorption of CO alone. The surface interaction between H_2 and CO_2 on supported Rh provided a good example of this: adsorbed CO and formate species were identified by infrared spectroscopy at 300–423 K, without any indication of the evolution of gaseous CO (*1, 2*). The spectral features of adsorbed CO produced by $H_2 + CO_2$ adsorption differed basically from those observed during the adsorption of CO on the sample: (i) the doublet due to $Rh(CO)_2$ was completely missing, and (ii) the band due to linearly bonded CO appeared at lower frequency, viz., 2020–2030 cm^{-1}.

The formation of formate species in the $H_2 + CO_2$ surface interaction could not be held responsible for this difference, as strong evidence has been presented that the formate species is located not on the Rh, but rather on the support (*1, 2*).

These results were interpreted by assuming that (i) the adsorbed H promotes the dissociation of CO_2, and (ii) Rh carbonyl hydride,  $Rh\begin{smallmatrix}H\\CO\end{smallmatrix}$ (or $Rh\begin{smallmatrix}CO\\-H\\CO\end{smallmatrix}$), is formed, which prevents the development of *gem*-dicarbonyl and causes a red shift of the Rh_x–CO band through extended electron donation. This interpretation was questioned by Iizuka and Tanaka and led to some controversy (*3–5*). However, the recent results of Worley *et al.* (*6*) using D_2 fully supported the above explanation.

Many of the above features were observed following the adsorption of H_2CO on Rh/Al_2O_3 (*7, 8*) in the decomposition of surface formate at 373–473 K on Rh supported by Al_2O_3, TiO_2, SiO_2, or MgO (*1, 2, 9*), and recently during the interaction of various organic compounds with supported Rh (*10*). In all these cases linearly bonded and bridge-bonded CO were formed in appreciable quantities. The species $Rh(CO)_2$ was absent, or present only in a small amount. In the interpretation of the unique spectrum of adsorbed CO, an important role was initially attributed to Rh carbonyl hydride (*7*).

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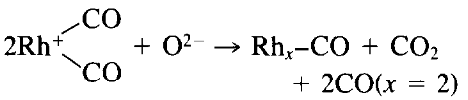
However, in a recent study of the adsorption of H_2CO and $(HCO)_2$ on Rh/Al_2O_3, the role of rhodium carbonyl hydride was completely neglected (*8*). As only very weak bands due to *gem*-dicarbonyl appeared in the spectrum, Yates and Cavanagh (*8*) came to the conclusion that H_2CO does not decompose appreciably on the isolated Rh sites, and that the slight shift observed in the $Rh(CO)_2$ doublet is due to the interaction of the $Rh(CO)_2$ with adsorbates produced by H_2CO on the Al_2O_3 support.

Recent spectroscopic measurements revealed several new features of the structure and topology of supported Rh (*11, 12*). EXAFS results clearly indicated that the Rh in 0.5% Rh/Al_2O_3 (reduction temperature, $R_T = 593$ K) is highly dispersed, but not dispersed like Rh atoms or ions; the metal crystallites consist of 15–20 rhodium atoms (*11*). The isolated Rh^+ sites, capable of binding two CO molecules, are formed due to the oxidative disrupting effect of CO. This conclusion was supported by detailed IR spectroscopic studies (*12*), which showed that in the case of highly dispersed Rh the disrupting effect of CO is very fast at 300 K, but it is observable even when Rh is present in larger crystallites ($R_T = 1273$ K). Traces of H_2O cause a promoter effect. Further, it was demonstrated that disruption of the Rh–Rh bonds does not require the presence of gaseous CO; it can proceed on the action of adsorbed CO (*12*). Van't Blik *et al.* (*11*) described this process by the equation

$$2Rh + 4CO + 2AlOH \rightarrow 2Al\text{–}O\text{–}Rh(CO)_2 + H_2. \quad (1)$$

Above 423 K, another effect of CO comes into prominence, which leads to the formation of Rh crystallites at the expense of isolated Rh^+ sites (*12*). This can be attributed to the reactions:



$$2Rh^{+}\langle^{CO}_{CO} + O^{2-} \rightarrow Rh_x\text{–}CO + CO_2 + 2CO(x = 2) \quad (2)$$

$$nRh_x\text{–}CO \rightarrow Rh_{n \cdot x}\text{–}CO + (n - 1)CO. \quad (3)$$

In the light of these findings, a reinterpretation of the surface processes responsible for the spectral features of adsorbed CO formed in the surface reaction is clearly required. In addition, we needed to seek an answer for the apparent nonoccurrence of the formation of *gem*-dicarbonyl (i.e., disruption of the Rh–Rh bonds) on the action of CO produced in a surface reaction, which otherwise proceeds easily.

EXPERIMENTAL

The experimental methods were the same as those used in our previous study (*2*). IR spectra were recorded with a Specord 75 IR double-beam spectrometer (Zeiss, Jena) with a resolution of ± 5 cm^{-1}. In certain cases difference spectra were produced and magnified with the help of a DATA system (Tracor Northern, TN 1710) interfaced directly to the Specord 75. Two different cells were used. In the high-temperature cell the spectra were taken at the adsorption temperature. In a Kiselev-type IR cell, all spectra were recorded at the temperature of the infrared beam, ~313 K (*9*). The cells were connected to a vacuum line and to a closed circulation system in which the gases were circulated during adsorption by a small magnetic pump.

The dispersion of the rhodium was determined via H_2 adsorption at 298 K through the use of dynamic impulse method (*1, 2*). Characteristics data on the supported Rh samples are shown in Table 1.

Rh/Al_2O_3 samples were prepared by incipient wetting of Al_2O_3 (Degussa, BET area 100 m^2/g) with an aqueous solution of $RhCl_3$. After impregnation, the samples were dried in air at 373 K.

For the IR studies, the dried Rh/Al_2O_3 powder was pressed into thin self-supporting wafers (30 × 10 mm, 20 mg/cm^2). The

TABLE 1

Adsorption of H_2 on Rh/Al_2O_3 at 300 K

Sample	Reduction temperature (K)	H/Rh
1% Rh/Al_2O_3	673	0.36
1% Rh/Al_2O_3	1273	0.10
2% Rh/Al_2O_3	673	0.34
5% Rh/Al_2O_3	673	0.30
5% Rh/Al_2O_3	1273	0.018

pretreatment of the samples was performed in the vacuum IR cell: the samples were (a) heated (20 K min^{-1}) to 573 K under constant evacuation; (b) oxidized with 100 Torr O_2 (1 Torr = 133.3 Pa) for 60 min at 573 K, (c) evacuated for 30 min, and (d) reduced with 100 Torr H_2 for 60 min at 573–1273 K. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. The gases were circulated during the oxidation and reduction processes.

The gases used were of commercial purity. CO_2 was purified by fractional distillation. CO (99.9%) was purified by bubbling through a $Mn(OH)_2$ suspension. Water vapor was frozen out by a trap cooled with a dry ice–acetone mixture. H_2 was purified by passage at the temperature of liquid air through a trap filled with molecular sieve.

RESULTS

1. CO_2 Adsorption

First, the spectral changes following the dissociation of CO_2 in the absence of H_2 were investigated. As the behavior of Rh/Al_2O_3 samples depends on the Rh content and on the reduction temperature, the adsorption of CO_2 was examined on different Rh/Al_2O_3 samples. Great care was taken to remove hydrogen from the surface, by prolonged degassing of the samples at the temperature of reduction, as omission of this can lead to false conclusions about the activity of Rh (*1*, *2*). The temperature range was restricted mainly to 300–423 K, as above 423 K the effect of the CO formed on the topology of the Rh is basically different from that exhibited at lower temperatures (*12*).

The adsorption of CO_2 (25 Torr) on poorly dispersed 5% Rh/Al_2O_3 (R_T = 1273 K) produced no observable spectral features in the CO frequency range at 300–423 K. Carbonate bands appeared at 1640, 1440, and 1230 cm^{-1}. The situation was similar for 1% Rh/Al_2O_3 (R_T = 1273 K).

When the temperature of reduction of the Rh samples was 573 or 673 K, we found a very weak signal at 2020 cm^{-1} for 5% Rh/Al_2O_3. This can be attributed to linearly bonded CO formed from the dissociation of CO_2. However, this weak band was detected only at or above 423 K (Fig. 1).

Attempts to increase its intensity and to detect formation of other species by increasing the pressure of CO_2 to 300 Torr, or by extending the adsorption time to 24 h, proved ineffective.

2. H_2 + CO_2 Coadsorption

The adsorption of H_2 + CO_2 (25 Torr each) on 5% Rh/Al_2O_3 (R_T = 673 K) produced spectral features at 2030 and 1850 cm^{-1}. In addition, new bands were identified at 1595, 1383, and 1375 cm^{-1} in the low-frequency region, in good agreement with those observed previously on Rh/Al_2O_3 (*1*). It is important to point out that there was no indication of the development of *gem*-dicarbonyl (Fig. 2).

When the temperature of reduction of the 5% Rh/Al_2O_3 was increased to 1273 K, the situation remained the same, but the intensities of the absorption bands were weaker (Fig. 2). Similar spectral features were observed following H_2 + CO_2 adsorption on Rh/Al_2O_3 containing only 1% Rh (Fig. 2).

For comparison we show the IR spectra obtained following CO adsorption on these Rh samples (Fig. 3). In the case of high-temperature-reduced samples (R_T = 1273

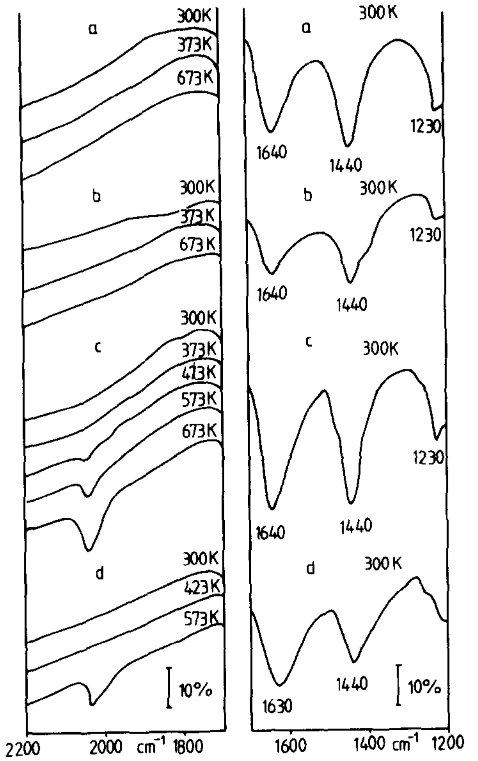


FIG. 1. Infrared spectra observed at 300 K following CO_2 adsorption at 50 Torr on Rh/Al_2O_3 samples at different temperatures. Adsorption time was 30 min. (a) 1% Rh/Al_2O_3, $R_T = 673$ K; (b) 1% Rh/Al_2O_3, $R_T = 1273$ K; (c) 5% Rh/Al_2O_3, $R_T = 673$ K; (d) 5% Rh/Al_2O_3, $R_T = 1273$ K.

K) the adsorption of CO initially yielded only bands of linearly bonded (2060 cm^{-1}) and bridge-bonded (1870 cm^{-1}) CO (Fig. 3). In contrast, the adsorption of CO on 1% Rh/Al_2O_3 at 300 K ($R_T = 673$ K) immediately produced intense bands of *gem*-dicarbonyl at 2100 and 2030 cm^{-1}, with no or only a very weak indication of the presence of linearly bonded and bridge-bonded CO (Fig. 3). When the Rh content was 5%, intense spectral features were observed due to Rh_x–CO, $Rh^+(CO)_2$, and Rh_2CO surface species (Fig. 3).

Spectral changes observed in the presence of $H_2 + CO_2$ were followed for up to 20–24 h, as we had observed previously that at low initial dispersion of Rh, development of the *gem*-dicarbonyl required a long contact time. This was particularly the case for the effect of adsorbed CO. As can be seen in Fig. 2, independent of the reduction temperature (i.e., of the size of the Rh crystallites), there was no sign of the development of *gem*-dicarbonyl in the coadsorption of $H_2 + CO_2$, even after a long adsorption time.

However, when the cell was degassed af-

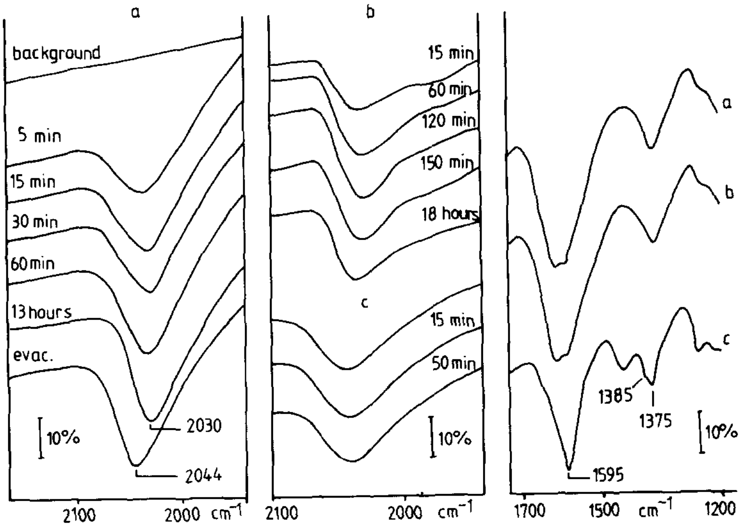


FIG. 2. Changes in the infrared spectra produced by $H_2 + CO_2$ (25 Torr each) coadsorption on Rh/Al_2O_3 at 373 K as a function of time. Spectra were taken at 300 K. (a) 5% Rh/Al_2O_3, $R_T = 673$ K; (b) 5% Rh/Al_2O_3, $R_T = 1273$ K; (c) 2% Rh/Al_2O_3, $R_T = 673$ K.

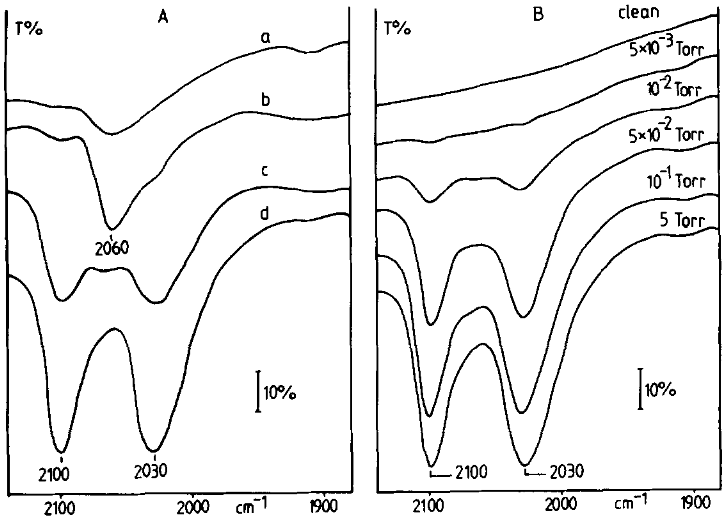


FIG. 3. Infrared spectra for CO adsorbed at 30 K on Rh/Al_2O_3. (A) In the presence of 5 Torr CO; (a) 1% Rh/Al_2O_3, $R_T = 1273$ K; (b) 5% Rh/Al_2O_3, $R_T = 1273$ K; (c) 5% Rh/Al_2O_3, $R_T = 673$ K; (d) 1% Rh/Al_2O_3, $R_T = 673$ K. (B) As a function of CO pressure, 1% Rh/Al_2O_3, $R_T = 673$ K.

ter the highest intensity of the Rh_x–CO band had been attained, significant spectral changes occurred. These are shown in Fig. 4. The 2030 cm^{-1} band slowly diminished in intensity and the band gradually shifted to higher frequencies after 90 min to 2044 cm^{-1}. The most important observation was that bands at 2100 and 2030 cm^{-1}, due to *gem*-dicarbonyl, also developed in the later stages (Fig. 4).

When the degassing was performed at higher sample temperatures, e.g., 373 K, the 2030-cm^{-1} band immediately shifted to 2040 cm^{-1}, and the *gem*-dicarbonyl bands appeared in the early stages. Further increase of the temperature led to a larger decrease in the intensity of the CO band, which made it more difficult to establish the spectral changes followed.

In order to demonstrate the effect of pure CO on the Rh sample used in this work we present Fig. 5. This clearly illustrates the development of *gem*-dicarbonyl in the presence of CO on the high-temperature-reduced Rh/Al_2O_3 sample as a function of time.

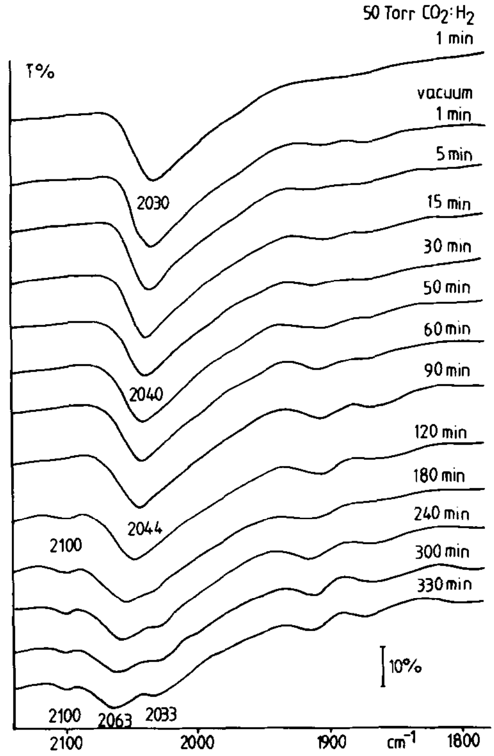


FIG. 4. Changes in the infrared spectrum of adsorbed CO (produced by the coadsorption of H_2 + CO_2 at 373 K) on 5% Rh/Al_2O_3 reduced at 673 K under vacuum.

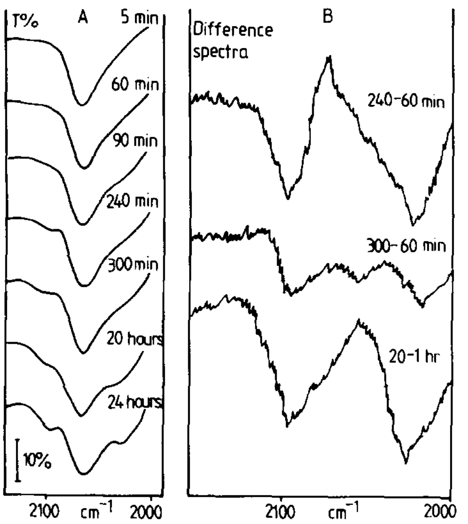


FIG. 5. (A) Changes in the infrared spectra of adsorbed CO on 1% Rh/Al_2O_3 reduced at 1273 K in the presence of 50 Torr of CO as a function of time at 300 K. (B) Difference spectra produced and magnified by a Tracor DATA system.

DISCUSSION

1. Spectral Changes Followed CO_2 Dissociation

Let us deal first with the dissociation of CO_2 and the resulting spectral changes. The question of the dissociation of CO_2 on Rh has been the subject of great controversy in the literature (*1–6, 13–22*). Recent studies did not confirm the dissociation of CO_2 on Rh(111) (*17–20*) or on Rh foil (*18, 19*) under ultrahigh vacuum (UHV) conditions, which is in accord with the theoretical calculations (*16, 17*). Dissociation of CO_2 was observed only when boron, a common impurity in Rh, segregated onto the Rh surface or in the presence of H_2 (*18, 19, 21, 22*).

Although the conditions for the dissociation of CO_2 are much more favorable on highly dispersed Rh at an elevated temperature and at 10–760 Torr (*16, 17*), the temperature of onset of dissociation still varies (*1–6, 21–23*). Consistent with our previous finding, we could discover no convincing evidence of the dissociation of CO_2 on Rh/Al_2O_3 at 300 K: we detected the formation of adsorbed CO only at or above 423 K. This is also in line with the recent results of Henderson and Worley (*21, 22*), who, although applying sensitive IR measurements, detected chemisorbed CO over 10% Rh/TiO_2 only at 503 K. In contrast, Primet (*23*) and Iizuka and Tanaka (*3, 5*) observed spectral changes indicative of the dissociation of CO_2 even at 300 K. Apart from these discrepancies, a common feature of all these studies is that, if the dissociation of CO_2 did occur, it produced only linearly bonded CO, at lower frequencies, viz., 2020–2030 cm^{-1}.

The question arises as to why only linearly bonded CO is produced in the dissociation of CO_2, while the adsorption of CO alone even at the lowest exposure on the same Rh samples (R_T = 673 K) yields mainly $Rh^+(CO)_2$, without Rh_x–CO and Rh_2CO species (Fig. 3B). Following the interpretation suggested for the spectral feature occurring during H_2CO adsorption (*8*), one can propose that the dissociation of CO_2 occurs on centers different from those involved in the adsorption of CO.

However, the results of recent EXAFS measurements showed that even a highly dispersed Rh sample contains no isolated Rh sites, but only metal crystallites, which in an optimum case consist of 15–20 Rh atoms (*11*). Thus, we cannot talk about basically different sites on the Rh surface. In other words, on the basis of the missing $Rh(CO)_2$ species we cannot conclude that the surface reaction occurs or does not occur on isolated Rh sites, as initially there are no such sites on the surface.

Consistent with our previous study (*12*) we demonstrated that the Rh clusters can be disrupted even by adsorbed CO (Fig. 4). Although the condition for the formation of isolated Rh^+ sites is more favorable following the oxidative dissociation of CO_2

$$CO_2 + Rh_x = Rh_{x-2}\text{–}CO + 2Rh^+ + O^{2-} \quad (4)$$

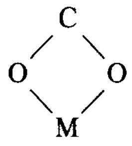
than during the adsorption of reductive CO, the disruption of Rh–Rh was not observed on the action of CO formed in CO_2 dissociation. One possible reason is that the extent of CO_2 dissociation, i.e., the surface concentration of CO, is too low to induce an observable disruption of the Rh–Rh bonds. The fact that linearly bonded CO remained the only surface species, even when its surface concentration was increased at elevated temperatures (400–673 K) by somewhat greater CO_2 dissociation (Fig. 1, and Refs. (*3, 4, 21*)), is not in contradiction with this explanation. We found that another effect of CO comes into prominence above 423 K, namely, the agglomeration of isolated Rh^+ into Rh_x crystallites (*12*). Hence the formation of *gem*-dicarbonyl could not be expected in the dissociation of CO_2 at or above 423 K.

An alternative explanation is that the dissociation of CO_2 occurred due to the promoting effect of H_2 impurity or the adsorbed hydrogen that had migrated from the support onto the Rh (inverse spillover), as suggested by Henderson and Worley (*21, 22*). This phenomenon is discussed in the following section.

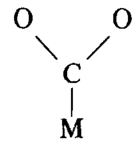
2. H_2 + CO_2 *Interaction*

In the coadsorption of $H_2 + CO_2$, the CO bands appeared at much higher intensities, indicating that hydrogen promotes the dissociation of CO_2. This effect was similarly established on the Rh(111) single-crystal surface under UHV conditions (*19*), but it was not observed on a Rh tip (*20*). However, a weak interaction was indicated by work function measurements in this case, too. In the interpretation of this feature we may speculate that in the presence of chemisorbed hydrogen CO_2 adsorbs in a form different from that on the clean surface.

The adsorption of CO_2 is weak on clean Pt metals. As photoemission studies indicated no energy shift on Pt and Cu surfaces (*24, 25*), Ray and Anderson (*26*) proposed bonding via a lone pair of an O atom of CO_2, with a linear molecular bond. The low-temperature desorption peak ($T_p \approx 110$ K) from clean Rh(111) very probably corresponds to this type of bonding. However, a more stable adsorption state was also observed (T_p = 240–260 K; E_{des} = 60 kJ/mol), indicating the bonding of CO_2 in other forms, e.g., with two oxygens or with the carbon atom:



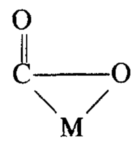
A



B

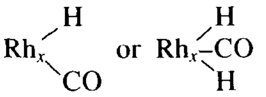
Adsorption and desorption studies published so far have not indicated that the bonding of CO_2 is different on highly dispersed Rh, and there is no evidence of chemisorbed CO_2 on Rh at 300 K and at ambient pressure.

However, we might expect that other adsorbed species, by donating electrons to the CO_2 π orbital through Rh, or in a direct surface interaction, change the surface configuration of CO_2 into a more stable bidentate structure:



C

This was probably the case for the CO_2 + K/Rh(111) and the CO_2 + K/Pd(100) systems (*27, 28*). Preadsorbed potassium dramatically increased the binding energy of CO_2 and lowered the activation barrier for dissociation in both cases.

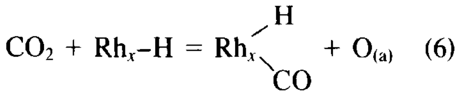
As adsorbed hydrogen can also donate electrons through the Rh it may promote the formation of partially negatively charged CO_2, i.e., the formation of the CO_2^- anion radical (the concentration of this species is very low, as there is no IR spectral feature that can be attributed to adsorbed CO_2^-). As a result the dissociation of CO_2 occurs or increases in extent. The absorption band of Rh_x–CO produced in the presence of H_2 appeared at lower frequencies than in the case of CO adsorption alone (the linearly bonded CO at 2030–2045 cm^{-1}, the bridge-bonded CO at 1830 cm^{-1}). The twin band indicative of the *gem*-dicarbonyl was again absent and, independently of the initial dispersion of Rh, did not develop even after a long adsorption time. Similar phenomena were observed following the adsorption of various organic compounds (*10*). We attribute these features to the presence of hydrogen and/or to the formation of rhodium carbonyl hydride, and exclude again the presence of different surface centers. The existence of this surface species seems to be supported by the spectral changes that occurred during the evacuation following the $H_2 + CO_2$ interaction at 373 K (Fig. 4). As the binding energy of H to Rh is less than that of CO, we expected that mainly H_2 would desorb at 373 K. This was actually the case, as the intensity of the CO band diminished only slightly during the degassing. A decrease in the CO coverage should lead to a decrease in absorption frequency due to the lower influence of dipole–dipole coupling. However, in the present case a change in the opposite direction occurred; the CO band was shifted to higher frequency. We consider this to be evidence of the existence of rhodium carbonyl hydride on the surface; the observed shift is a result of the loss of hydrogen, and the partial transformation of  $\mathrm{Rh}_x\begin{array}{l}\diagup\mathrm{H}\\ \diagdown\mathrm{CO}\end{array}$ or $\mathrm{Rh}_x\begin{array}{l}\diagup\mathrm{H}\\ -\mathrm{CO}\\ \diagdown\mathrm{H}\end{array}$ to Rh_x–CO species. This transformation leads to the diminishing effect of adsorbed hydrogen on the position of the CO band, which overcompensates the effect of the decrease in the CO coverage.

The fact that the bands due to *gem*-dicarbonyl started to develop after the gradual removal of adsorbed H by prolonged evacuation at 300 K, i.e., after disruption of the Rh–Rh bonds began, clearly shows that the adsorbed H prevents the disrupting effect of CO formed in the $H_2 + CO_2$ surface interaction.

On the basis of above considerations we propose the following steps to describe the spectral changes observed in the surface interaction of H_2 and CO_2 on Rh/Al_2O_3 at 300 K.

Adsorption and dissociation of H_2 and CO_2 at 373 K:

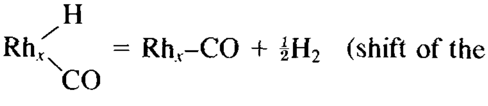
$$\tfrac{1}{2}\mathrm{H}_2 + \mathrm{Rh}_x = \mathrm{Rh}_x\text{–H} \qquad (5)$$



$$\mathrm{CO}_2 + \mathrm{Rh}_x\text{–H} = \mathrm{Rh}_x\begin{array}{l}\diagup\mathrm{H}\\ \diagdown\mathrm{CO}\end{array} + \mathrm{O}_{(a)} \qquad (6)$$

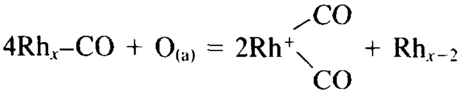
(development of a band at 2020–2035 cm^{-1}).

Desorption of H_2 during evacuation at 300–373 K:



$$\mathrm{Rh}_x\begin{array}{l}\diagup\mathrm{H}\\ \diagdown\mathrm{CO}\end{array} = \mathrm{Rh}_x\text{–CO} + \tfrac{1}{2}\mathrm{H}_2 \quad \text{(shift of the band to 2030–2045 cm}^{-1}\text{).} \qquad (7)$$

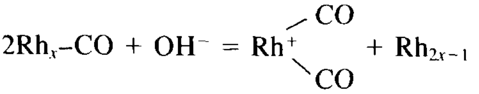
Oxidative disruption of Rh_x with the oxygen formed from the CO_2 dissociation:



$$4\mathrm{Rh}_x\text{–CO} + \mathrm{O}_{(a)} = 2\mathrm{Rh}^{+}\begin{array}{l}\diagup\mathrm{CO}\\ \diagdown\mathrm{CO}\end{array} + \mathrm{Rh}_{x-2} + \mathrm{O}^{2-} + 3\mathrm{Rh}_x$$

(slow development of the $Rh^{+}(CO)_2$ bands at 2100 and 2030 cm^{-1}). (8a)

Oxidative disruption of Rh_x with adsorbed CO and support OH:



$$2\mathrm{Rh}_x\text{–CO} + \mathrm{OH}^{-} = \mathrm{Rh}^{+}\begin{array}{l}\diagup\mathrm{CO}\\ \diagdown\mathrm{CO}\end{array} + \mathrm{Rh}_{2x-1} + \mathrm{O}^{2-} + \tfrac{1}{2}\mathrm{H}_2$$

(slow development of the $Rh^{+}(CO)_2$ bands at 2100 and 2030 cm^{-1}). (8b)

In the above reaction scheme we assume that the dissociation of CO_2 (i.e., the production of adsorbed CO) occurs through the formation of a bent CO_2 structure on the Rh (form C) induced by an electron donation from adsorbed hydrogen via Rh into the CO_2 π orbital. An alternative route is that adsorbed CO is formed in the decomposition of formate species at the Rh/support interface. Although previous results strongly suggested that stable formate species (detected also in the present case, see Fig. 2) locates exclusively on the support (*1, 2, 9*), at higher temperatures (~473 K) it can migrate to the Rh where it decomposes catalytically. However, it is highly unlikely that the contribution of this reaction is important in the formation of adsorbed CO in the $H_2 + CO_2$ surface interaction at 300–423 K, as adsorbed CO is produced at same concentration on Rh/SiO_2, where we can absolutely rule out the existence of formate species.

It is evident from the Introduction and from the above discussion that the presence of isolated Rh^+ sites plays a key role in the production of *gem*-dicarbonyl. Although several proposals have been suggested for the oxidation of Rh clusters on the support, we feel that the mechanism of the formation of Rh^+ sites is still not unambiguously solved.

The most probable route is the oxidation of Rh crystallites by an OH group of the support during carbonylation (Eq. (1)), as described by van't Blik *et al.* (*11*). This proposal was based on the finding that surface hydroxyl on Al_2O_3 is effective in converting $Rh_6(CO)_{16}$ to a species in which the Rh^0 in the carbonyl is oxidized to Rh^+ (*30, 31*). Our observations that the formation of isolated Rh^+ sites (on which $Rh^+(CO)_2$ forms) proceeds more slowly under dry conditions, and that moisture accelerates this process, support this explanation (*12*).

van't Blik *et al.* (*32, 33*) recently favored the idea, which was suggested first by Primet (*23*), that Rh crystallites are oxidized by dissociatively adsorbed CO molecules at 300 K. However, our more detailed studies provided no evidence for the dissociation of CO on supported Rh at 300–400 K, but clearly indicated the occurrence of this process (for the first time to our knowledge) at higher temperature, ≥473 K (*34–36*).

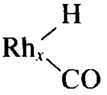
A decisive experimental observation against the role of CO dissociation in the production of isolated Rh^+ sites is that the formation of $Rh^+(CO)_2$ species occurs even at low temperature, ~170 K (*23, 37*), when the dissociation of CO is highly improbable. One can argue that the Rh^{3+} on the support is not fully reduced to metal during the preparation, and a significant portion is retained in a higher oxidation state (*38–41*). This was demonstrated recently by Jackson (*41*), who studied the adsorption and temperature-programmed thermal desorption of CO on supported Rh. However, as was pointed out (*41*), his samples were not calcined in air at high temperature before reduction, which is probably necessary to attain a complete reduction. Although the preparation of the samples and the nature of the supports can strongly influence the properties of supported rhodium catalysts, data accumulating in the recent past indicate that the reduction of preoxidized Rh is complete at 573–673 K (*33, 42, 43*). It is important to emphasize that the oxidative disruption of the Rh clusters (i.e., the slow formation of *gem*-dicarbonyl) has been observed after reduction of Rh/Al_2O_3 at 1273 K (*12*) (see Fig. 5).

An alternative possibility is that an electronic interaction occurs between small Rh crystallites and the alumina support, leading to partially charged Rh. Hyde *et al.* (*44*) described the formation of cationic Rh on oxide support in this way as some electron transfer from the Rh to the supporting oxides had been detected by ESCA measurements. Although we sympathize with this view, and indeed one of us presented the first experimental observation for this type of electronic interaction in the case of Ni/TiO_2 (*45–47*), we feel that the formation of Rh^+, at least on other supports of different electronic character (e.g., on titania and silica), cannot be explained by this model. Further studies are in progress in our laboratory on this subject.

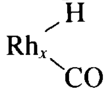
CONCLUSIONS

1. No evidence was found for the dissociation of CO_2 at 300 K on low- or high-temperature-reduced Rh/Al_2O_3. A very weak CO band at 2020–2025 cm^{-1}, indicative of

the dissociation of CO_2, was observed only at and above 423 K.

2. The presence of hydrogen increased the dissociation of CO_2, which was exhibited by the enhanced intensity of the band at 2020–2030 cm^{-1}, due to Rh_x–CO and  $\mathrm{Rh}_x{<}^{\mathrm{H}}_{\mathrm{CO}}$ species.

3. Features of *gem*-dicarbonyl were completely absent in both cases, indicating the absence of disruption of the Rh–Rh bond.

4. However, disruption of the Rh–Rh bond proceeded gradually after decomposition of the  $\mathrm{Rh}_x{<}^{\mathrm{H}}_{\mathrm{CO}}$ species by partial removal of the adsorbed hydrogen.

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