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Infrared Spectroscopic Study of the Adsorption and Reactions of CO_2 on K-Modified Rh/SiO_2

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Adsorption of CO_2 on K-free Rh/SiO_2 at 140 K produced only a strong band at 2340 cm^{-1} characteristic of weakly bonded CO_2. There was no carbonate formation and CO_2 desorbed completely from this surface below 250 K without any detectable dissociation. Co-adsorption of H_2 + CO_2 on Rh/SiO_2 led to the formation of CO bands at 2050 and 2015 cm^{-1}, indicating the dissociation of CO_2. Formate bands were not observed. Adsorption of CO_2 on K-modified Rh/SiO_2 produced an intense band at 1695–1675 cm^{-1} and a weak band at 1325–1360 cm^{-1}, which are attributed to the formation of CO_2^- anions bonded to K^+ ions. Spectral changes observed above 200 K suggest that this species is transformed into bidentate carbonate characterized by absorption bands at 1660, 1525, and 1360 cm^{-1}. As the same features were observed for Rh-free samples, it was concluded that both species are coordinated to K^+-sites on the silica surface. CO_2^- reacted with hydrogen on $(K + Rh)/SiO_2$ to give formate at temperatures as low as 150 K. No formate was produced on K/SiO_2 in the absence of Rh. © 1990 Academic Press, Inc.

1. INTRODUCTION

The influence of alkali metal adatoms on the adsorption and reactivity of various gaseous molecules such as CO, CO_2, and NO on metal surfaces has recently attracted increasing attention. Drastic changes were observed when alkali atoms were co-adsorbed mainly on single-crystal metal surfaces which consisted of (i) a marked increase in the binding energy of adsorbed molecules, (ii) a significant decrease in the characteristic absorption bands of adsorbed species (e.g., CO), and (iii) enhancement of the dissociation probability (*1*). In the case of supported metals, the effects were much less pronounced. This is due mainly to the large surface area of the supports which may prevent direct contact between the dispersed metals and alkali additives.

In the present work, the effect of potassium on the adsorption of CO_2 on supported Rh has been investigated using infrared spectroscopy. The interaction of CO_2 with both supported Rh and Rh single-crystal surfaces has been studied earlier in great detail (*2–13*). It is clear now that, independent of the state of the Rh, the adsorption of CO_2 is weak and molecular: adsorbed CO_2 desorbs completely from Rh surfaces below room temperature. However, potassium adlayers on a Rh (111) surface changed the structure of adsorbed CO_2, dramatically increased its binding energy, and caused the dissociation of CO_2 even below room temperature (*7, 13*).

The aim of our present study is twofold: (i) to examine whether the activation of CO_2 by potassium also proceeds on supported Rh, and (ii) to determine the reactivity of activated CO_2 toward hydrogen. For this purpose we used a larger amount of Rh, namely 10%, applied silica as a support (on which CO_2 adsorbs only weakly), and performed the experiments at low temperature.

2. EXPERIMENTAL

The catalyst precursor was obtained by adding the silica support (Aerosil from De-

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gussa, 200 m^2/g) to an aqueous solution of rhodium nitrate. The impregnated sample was dried at 400 K and decomposed in air at 573 K. The total metal content of this Rh/SiO_2 was 10 wt%. A portion of this solid material was then added to a solution of potassium nitrate and stirred. The material was evacuated to dryness under reduced pressure. The K weight percentage was 3%. K/SiO_2 was prepared in the same way using Rh-free SiO_2.

Self-supporting wafers (15–20 mg/cm^2) of the catalyst precursor samples were decomposed at 573 K *in situ* under continuous evacuation at 573 K for 1 h, oxidized under 150 Torr O_2 (1 Torr = 133.3 Pa) for 30 min and evacuated at 573 K for 30 min, heated in flowing hydrogen (50 ml/min; Linde, 99.997% nominal purity) up to 773 K, and kept at this temperature for 1.5 h. This treatment was followed by degassing at 573 K for 30 min; afterwards the sample was cooled to the adsorption temperature.

Infrared transmission spectra were measured with a Perkin–Elmer spectrometer Type 580 B. The wavenumber accuracy was better than ± 2 cm^{-1}; the spectral slit width was 5.3 cm^{-1}. The *in situ* cell used has been described previously (*14, 15*). The design of this cell permitted spectra to be recorded without contributions from the gas phase.

3. RESULTS

3.1. Adsorption of CO_2 on Rh/SiO_2

Adsorption of CO_2 on a K-free Rh/SiO_2 sample at 140 K produced a strong asymmetric band centered around 2340 cm^{-1}. This band disappeared on warming the sample to ~250 K in the presence of CO_2. It is important to note that there was no detectable spectral feature in the frequency range 1300–2200 cm^{-1} at temperatures up to 300 K which might have indicated the formation of carbonates or adsorbed CO.

The spectral characteristics were the same in the presence of hydrogen (80 Torr H_2 and 40 Torr CO_2) up to about 230 K. However, above this temperature a weak shoulder was clearly detected at 2045 cm^{-1} which was transformed into a well-developed band at 255–300 K (Fig. 1). In this temperature range there was a weaker band at 2015 cm^{-1} and the broadening of the absorbance due to SiO_2 at 1875 cm^{-1} could also be observed.

3.2. Adsorption of CO_2 on K-Modified Samples

(*a*) *(K + Rh)/SiO_2*. In contrast to the previous K-free sample, a new strong band at 1695 cm^{-1} was produced on $(K + Rh)/SiO_2$ at temperatures as low as 133–150 K in addition to the characteristic CO_2 band at 2345 cm^{-1}. Upon raising the temperature, the 1695-cm^{-1} band gained intensity and a very weak band at 1325 cm^{-1} was also detected. At 166 K another absorption band developed at 1525 cm^{-1} (Fig. 2). Its intensity increased slightly with rise in temperature. Above 200 K, the 1695-cm^{-1} band gradually broadened, moved to 1675 cm^{-1}, and was accompanied by a shift of the weak band from 1325 to 1355–1375 cm^{-1}. Evacuation of the sample at 300 K caused a complete elimination of the 1675 and 1360 cm^{-1} bands and left a weak band around 1660 cm^{-1}. No changes occurred with the 1525 cm^{-1} band.

(*b*) *K/SiO_2*. Adsorption of CO_2 on K-modified SiO_2 at 143 K after identical pretreatments also produced a very intense absorption band at 1695–1700 cm^{-1} and a weaker band around 1325 cm^{-1} (Fig. 3). Upon heating the sample, the first change occurred at 230 K: the 1700-cm^{-1} band shifted to 1685 cm^{-1} and the development of new bands, a stronger one at 1630 and a weaker one at 1410 cm^{-1}, was also observed. The band at 1320 cm^{-1} shifted to 1355 cm^{-1}. No further spectral changes occurred up to 300 K. Evacuation at this temperature somewhat attenuated all absorption bands but it did not eliminate any of them. This required elevated temperature of at least 500 K.

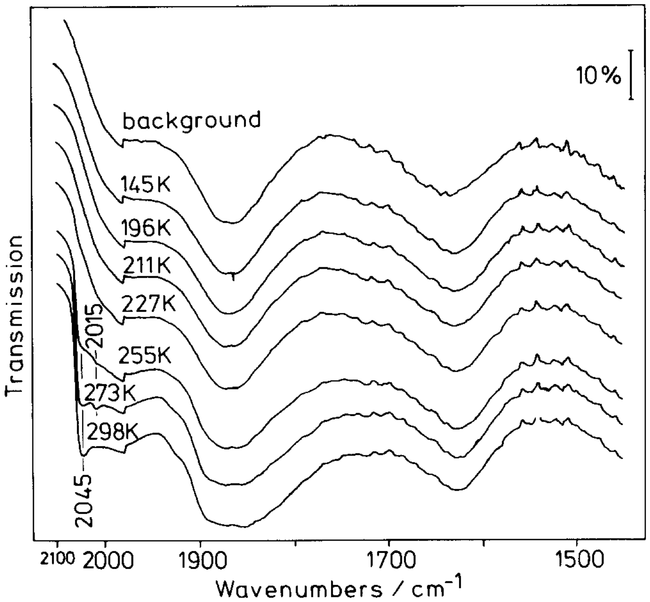


FIG. 1. Infrared spectra of 10% Rh/SiO_2 following H_2 (80 Torr) + CO_2 (40 Torr) co-adsorption at different temperatures. The reduced sample was first exposed to H_2 at 513 K, then cooled to ~140 K, after which CO_2 was admitted.

3.3. H_2 + CO_2 co-adsorption on K-Modified Rh/SiO_2

(*a*) *K* + *Rh/SiO*$_2$. In the first series of experiments, the interaction between activated hydrogen and CO_2 was followed, starting at low temperature. To ensure the formation of Rh–H species, 40 Torr H_2 was admitted to the sample after reduction at 773 K and outgassing at 573 K. The sample

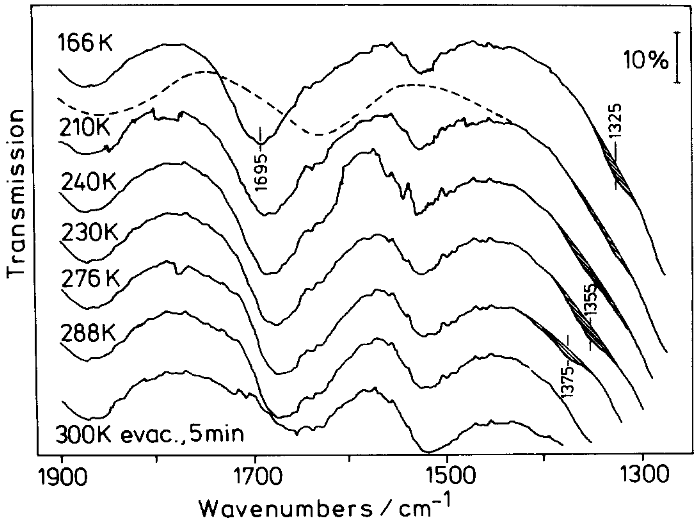


FIG. 2. Infrared spectra of (10% Rh + 3% K)/SiO_2 following CO_2 (40 Torr) adsorption at different temperatures. The reduced sample was exposed to CO_2 around 140 K and warmed to higher temperatures.

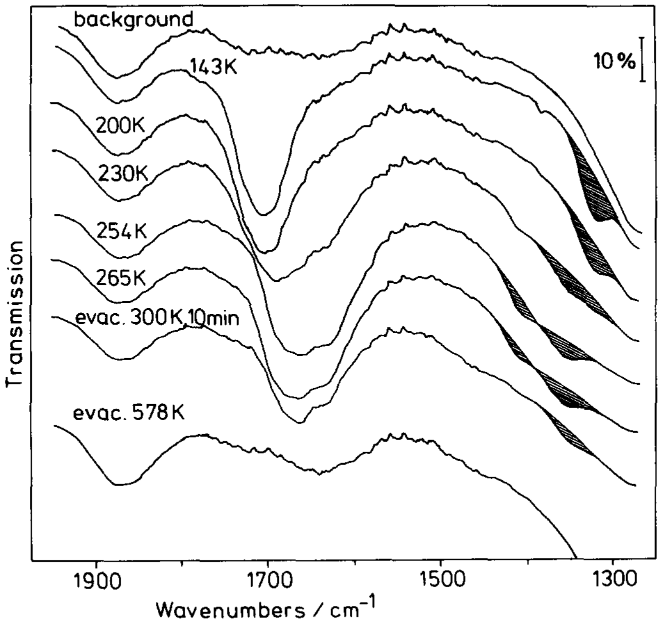


FIG. 3. Infrared spectra of 3% K/SiO_2 following CO_2 (40 Torr) adsorption at different temperatures. The reduced sample was exposed to CO_2 around 140 K and warmed to higher temperatures.

was then cooled in hydrogen from 573 K to 130–150 K. Admission of CO_2 (40 Torr) onto the sample produced an intense band at 1690 cm^{-1} and a less intense band at 1600 cm^{-1} (Fig. 4). The lowest temperature at which the 1600-cm^{-1} band developed was 150 K. Weak bands could also be detected at 1360 cm^{-1}. In the CH stretching region, the background spectrum showed weak bands at 2850, 2925, and 2965 cm^{-1}. Their

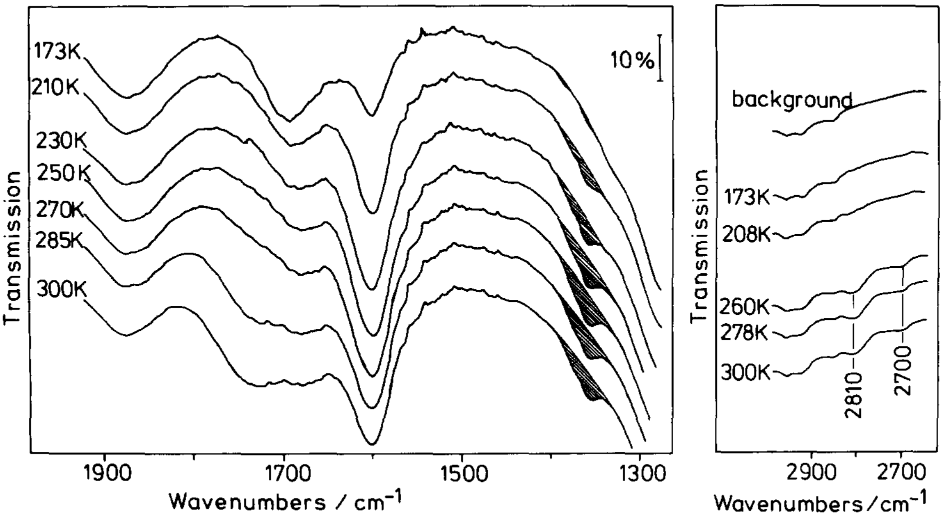


FIG. 4. Infrared spectra (10% Rh + 3% K)/SiO_2 following H_2 (80 Torr) and CO_2 (40 Torr) coadsorption at different temperatures. The reduced sample was first exposed to H_2 at 573 K, then cooled to ~140 K, after which CO_2 was admitted.

intensities remained constant during the subsequent experiments.

Upon raising the sample temperature, the 1690-cm^{-1} band shifted to 1675 cm^{-1} and gradually lost intensity. In contrast, the 1600- and 1360-cm^{-1} bands intensified and two weak bands developed at 2700 and 2810 cm^{-1} (see Fig. 4). A significant change occurred above 270 K, when a broad spectral feature developed at 1725–1730 cm^{-1} which gained intensity at 300 K.

In order to see whether the new bands could also be produced from surface species remaining adsorbed at 300 K, in the next experiment hydrogen was admitted to Rh/SiO_2 which was predosed with CO_2 at 300 K. The sample was degassed for 5 min before hydrogen admission at 300 K. The spectrum showed bands at 1660 and 1525 cm^{-1} (Fig. 5A). On admission of hydrogen a very weak band was produced at 1600 cm^{-1}, the previous broad band at 1660 cm^{-1} broadened further, and the band at 1525 cm^{-1} was completely eliminated. On raising the temperature to 373 K in the presence of hydrogen, the 1660-cm^{-1} band also disappeared and a new band developed at 1725 cm^{-1}. There was no indication of any CO bands in the range 1800–2100 cm^{-1}. After evacuation of the hydrogen a broad band remained at 1720 cm^{-1}. Admission of CO_2 (40 Torr) to the cell at 300 K further broadened this band which seems to be composed of two bands with maxima around 1720 and 1670 cm^{-1}. Addition of hydrogen to the CO_2 (H_2 : 80 Torr, CO_2 : 40 Torr) intensified the 1720-cm^{-1} band and produced an intense band at 1600 cm^{-1} and a weak shoulder at 1360 cm^{-1}. Keeping the sample in this gas atmosphere overnight enhanced the broad band and shifted it to 1780 cm^{-1} (Fig. 5B). The bands at 1600 and 1360 cm^{-1} also intensified slightly.

As regards the stability of these bands, the 1600- and 1360-cm^{-1} peaks disappeared even after evacuation at 383 K, whereas the broad band at 1780 cm^{-1} attenuated only above 423 K. The background spectrum was restored only at 673 K.

(*b*) *K/SiO_2*. In contrast to the $(K + Rh)/SiO_2$ sample, co-adsorption of $H_2 + CO_2$ on the Rh-free sample produced the same spectral features as those observed with CO_2 adsorption alone (Fig. 6). There was no indication of absorption bands, neither at 1600 nor at 1720 cm^{-1} at any temperature.

4. DISCUSSION

4.1. *Vibrational Characteristics of CO_2*

CO_2 is a linear molecule ($D_{\infty 4}$ symmetry) with three fundamental vibrations, namely, one Raman active ν_1 (symmetric stretching) which appears as a doublet at 1285 and 1388 cm^{-1} due to Fermi resonance with the overtone $2\nu_2$, and two infrared active vibrations, i.e., the doubly degenerate deformation ν_2 at 667 cm^{-1} and the antisymmetric stretching ν_3 at 2349 cm^{-1} (*16*). As regards the infrared spectrum of adsorbed CO_2, the following three cases can be distinguished.

(i) On unreactive surfaces the infrared spectrum of adsorbed CO_2 shows mostly the ν_3 vibration at 2349 cm^{-1}.

(ii) On reactive surfaces the adsorption of CO_2 may lead to the formation of several adsorbed species, such as carbonate, bicarbonate, and formate, which are characterized by different sets of absorption bands (*17, 18*). Depending on their coordination, four different forms of carbonates, i.e., symmetric, unidentate, bidentate, and bridged species, can be distinguished. The distinction among these forms can be made on the basis of the splitting of the ν_3 vibra-

TABLE 1

$\Delta\nu_3$ Splitting for Different Forms of Carbonates (*18*)

$\Delta\nu_3$ (cm^{-1})	Type of coordination
Zero	Symmetrical
100	Monodentate
300	Bidentate
400 or higher	Bridged

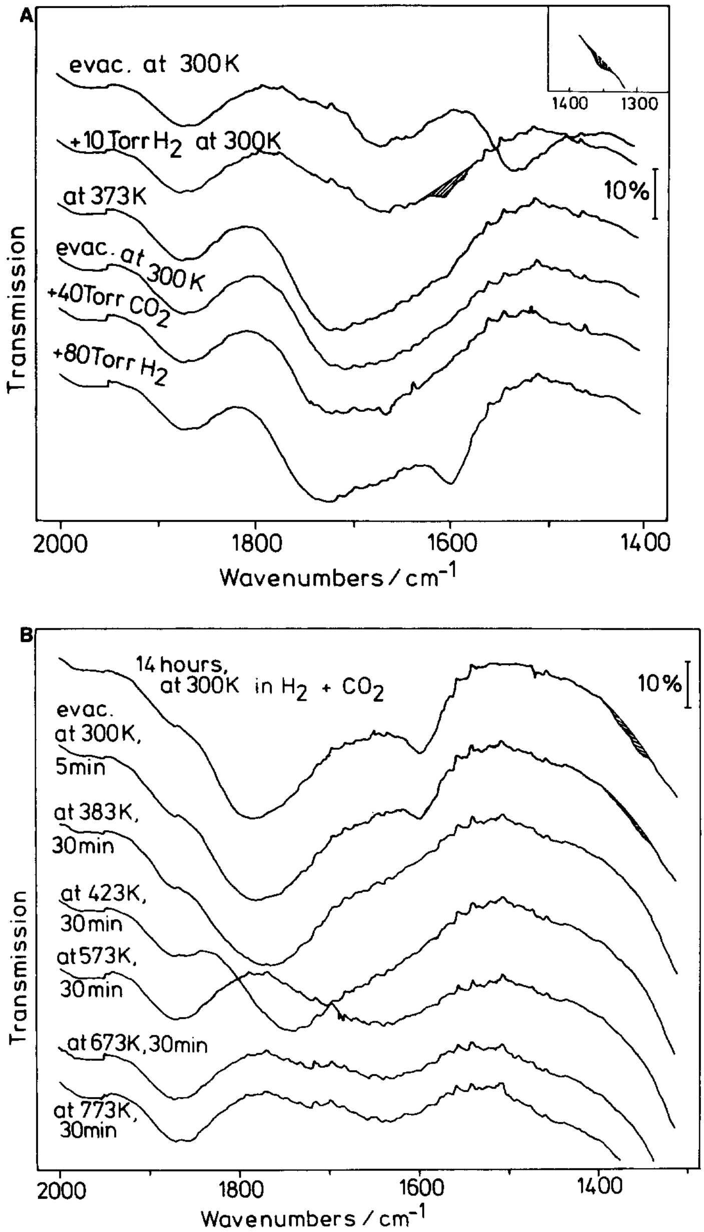


FIG. 5. (A) Spectral changes observed following H_2 admission to adsorbed CO_2 on (10% Rh + 3% K)/SiO_2, evacuation, and readsorption of H_2 and CO_2 at 300 K. (B) Spectral changes observed after keeping the sample in H_2 (80 Torr) and CO_2 (40 Torr) overnight and after evacuation at 300–773 K.

tion ($\Delta\nu_3$) (*17*) (Table 1). Bicarbonate ions exist in two forms, namely monomeric and dimeric.

(iii) CO_2 can also function as a ligand in different complexes of transition metals where its structure is strongly perturbed. Structures observed by X-ray diffraction are illustrated in Fig. 7. These carboxylate species have a characteristic pair of absorption bands in the 1700- to 1200-cm^{-1} region.

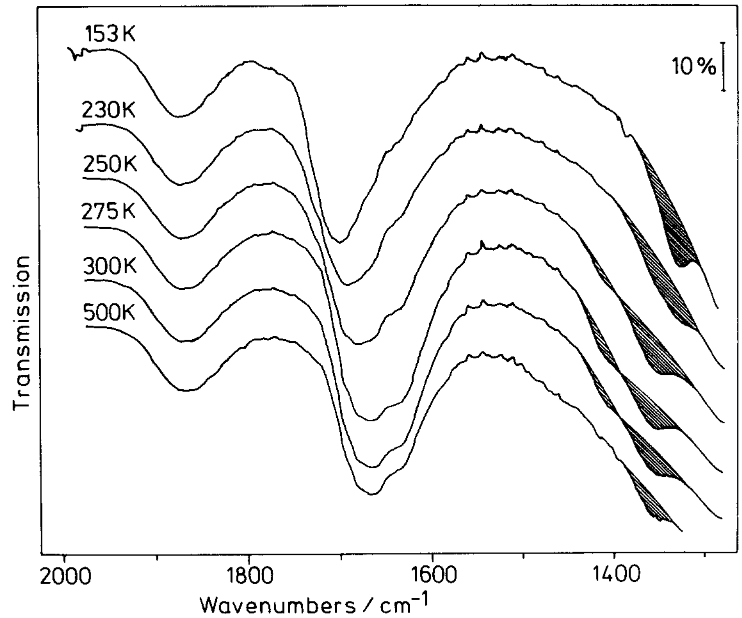


FIG. 6. Infrared spectra of 3% K/SiO$_2$ following H$_2$ (80 Torr) and CO$_2$ (40 Torr) co-adsorption at different temperatures; the procedure was the same as that in Fig. 5.

These latter bonding modes of CO$_2$ very probably occur when electrons are donated to the CO$_2$ molecule and a CO$_2^-$ anion is formed. The CO$_2^-$ ion has been identified so far under irradiation of sodium formate (absorption bands at 1675 and 1414 cm^{-1}) (*19*) and in the interaction of alkali metals with CO$_2$ in an argon matrix (absorption bands at 1568–1609 and 1325–1350 cm^{-1}) (*20, 21*). Work function measurements, photoemission, and electron energy loss spectra also suggested its presence on K-dosed Rh(111), Pd(100), and Pt(111) surfaces (*7, 13, 22, 23*). Its existence was also established on a more reactive clean Ni surface (absorption bands at 1620 and 1130 cm^{-1}) (*24–26*).

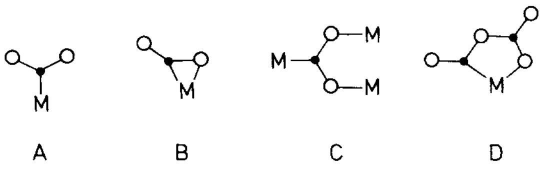
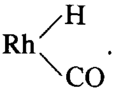


FIG. 7. Structures of CO$_2$ in complexes as identified by X-ray diffraction (*18*).

4.2. CO$_2$ Adsorption on Potassium-Free Samples

In the infrared spectra of adsorbed CO$_2$ on Rh/SiO$_2$ we observed only the ν_3 vibration at 2340 cm^{-1} at low temperatures, which indicates that the CO$_2$ molecule is only slightly perturbed and weakly adsorbed on this surface. The ν_2 vibration could not be detected as it occurs in the strong absorbance region of the support. The 2340-cm^{-1} band was eliminated by warming the adsorbed layer to 250 K without producing any new absorption bands which would have been indicative of the formation of adsorbed CO and/or carbonate species. This behavior is in agreement with previous observations which indicated that CO$_2$ does not dissociate on supported Rh at temperatures below 300 K (*8–12*). Also, carbonates are not formed on pure silica surfaces (*27, 28*).

The situation was the same in the presence of hydrogen up to 227 K. However, above this temperature a weak band appeared at 2050 cm^{-1}, the intensity of which grew as the adsorption temperature was increased. This band can be attributed to the formation of a linearly bonded CO on Rh_x crystallites. This result supports the view that adsorbed hydrogen can assist the dissociation of CO_2 on Rh (*8–10*). Analysis of the spectra in the 1800- to 1900-cm^{-1} region suggests that bridging CO which absorbs at 1875 cm^{-1} is also formed at 255 K. Another linearly bonded CO absorbing at 2015 cm^{-1} was identified at 255–273 K. The position of this CO band suggests that CO is strongly perturbed by hydrogen, very probably in the form of a Rh carbonyl hydride,  $\mathrm{Rh}{<}^{\mathrm{H}}_{\mathrm{CO}}$. The formation of this species has been observed and discussed in detail in previous papers (*8–10, 29, 30*).

4.3. Potassium-Modified Samples

The situation was completely different in the case of K-modified Rh/SiO_2, which can be considered a reactive surface. In this case, as is demonstrated in Fig. 2, an intense new band appeared at 1695 cm^{-1} and a weaker band at 1325 cm^{-1} at temperatures as low as 133–150 K, simultaneously with the major band at 2345 cm^{-1}. Above 200 K, the 1695-cm^{-1} band shifted to lower frequencies and at least four absorption bands, at 1675, 1630, 1525, and 1360 cm^{-1}, can be distinguished. Accordingly, the presence of potassium basically changed the adsorptive properties of the surface and hence the structure and bonding of CO_2 on this sample. The assignment of these absorption bands is based on characteristic vibrations observed previously following CO_2 adsorption on metals and oxides (*18*).

Spectral features observed below 200 K. The first aspects to be discussed will be the intense absorption band at 1695 cm^{-1} and the weak band at 1325 cm^{-1} (produced by low-temperature adsorption of CO_2), which were practically unchanged up to 170 K. For assignment of these bands, we can certainly exclude the formate species, as the positions of these bands are basically different from those of formate species on this and on other systems (*18*). The formation of carbonate species is also unlikely. The observed difference of the high- and low-frequency bands ($\Delta\nu_3$) is 365 cm^{-1}, which is significantly larger than the value attributed to monodentate and bidentate carbonates and smaller than that corresponding to the bridged form (Table 1). In addition, the species responsible for the 1695-cm^{-1} band seems to exhibit low thermal stability and apparently it transforms into another species at 166–200 K, which is not characteristic for carbonates of any type.

Taking this behavior into account, we believe that the 1695- and 1325-cm^{-1} bands are connected with the formation of the CO_2^- anion radical. The 1695-cm^{-1} band would be the antisymmetric stretch and the very weak band at 1325 cm^{-1} the symmetric stretch of CO_2^- species. As this pair of bands was also observed on the Rh-free surface we assume that the CO_2^- species is bonded to K^+ ions located on the silica surface. The possible structure is monodentate or bidentate (Fig. 7A or 7B). As regards the relatively high position of the antisymmetric stretching band we point out that in a study of the interaction of CO_2 and potassium metal Kafafi *et al.* (*21*) also observed a high-frequency band at 1689 cm^{-1} in N_2 matrix at high K/CO_2 ratio and attributed it to the formation of $K_nCO_2^-$ species (the most likely value for n was assumed to be 3). The position of the band was explained by a limited electron transfer between the potassium cluster and CO_2.

In this respect we refer to the work of Praliaud *et al.* (*31*) who performed XPS measurements with K-modified Ni/SiO_2 systems. Although the reduction of the nickel sample required high temperature (the maximum temperature attained during dynamic reduction was 923 K), there is no doubt that potassium remained in an oxidized form after the reduction. XPS-binding energy shifts to lower energies for Ni ($2p_{3/2}$) were reported as being induced by the presence of potassium, and a shift of the Curie point of the Ni was observed. Both phenomena were thought to be the result of an electron transfer from the potassium additive to Ni metal. The electron donation was attributed to the simultaneous effect of K^+ and O^{2-} taking into account that K^+ alone would hardly release electrons (ionization potential of K^+ is 31.7 eV). The electron-donating character of potassium and oxygen overlayers has been considered by others as well (*32–36*).

We may expect a similar phenomenon and electron donation to the CO_2 molecule in the present system, too. The electron transfer can occur through Rh metal; however, this way seems less important as the 1695- and 1325-cm^{-1} bands were also produced on potassium modified silica, e.g., on the Rh-free surface (Fig. 3). This suggests a direct electron transfer between CO_2 and potassium oxide.

It should be mentioned that the adsorption of CO_2 on K_2O–Ni/SiO_2 at 300 K produced infrared bands at exactly the same frequencies, at 1695 and 1325 cm^{-1}, as those in the present study, which transformed into 1665- and 1325-cm^{-1} bands after evacuation at room temperature (*31*). These bands were assigned to bidentate carbonate; the formation of the CO_2^- ion was not considered. As the CO_2^- species has been detected on clean Ni single-crystal surfaces even in the absence of electron-donating promotors (*24, 25*), it is not unlikely that the pair of bands at 1695 and 1325 cm^{-1} on K-modified Ni/SiO_2 was also the result of the production of the CO_2^- anion.

The formation of CO_2^- anions was previously assumed to occur on a fully decomposed 9-wt% K_2CO_3/Al_2O_3 sample (*37*). Adsorption of CO_2 produced two sets of bands at 1570 and 1320 cm^{-1} and 1590 and 1320 cm^{-1}, respectively. The former pair was attributed to bidentate carbonate, while the latter was assigned to a CO_2^- anion. However, the pair of bands at 1590 and 1320 cm^{-1} exhibited a remarkable stability; it existed even at 673–773 K which, taking into account the low thermal stability of CO_2^- anions on solid surfaces (*7, 13, 22–26*), makes this assignment very unlikely.

Different spectral features were observed in a study of the thermal treatment of K_2CO_3/Al_2O_3 at 300–570 K and above 570 K (*14*). In the lower temperature range strong bands appeared at 1350, 1410, and 1560 cm^{-1} and weak features at 1090 and 1825 cm^{-1}. Above 570 K bands were seen at 1350, 1420, and 1560 cm^{-1}. The 1410- and 1350-cm^{-1} bands (band splitting $\Delta\nu_3 = 60$ cm^{-1}) were attributed to monodentate carbonates, while the bands at 1560 and 1350 cm^{-1} ($\Delta\nu_3 = 210$ cm^{-1}) and at 1420 cm^{-1} were ascribed to bidentate carbonates (*14*).

Spectral features observed above 200 K. Spectral features observed above 200 K (Figs. 2 and 3) suggest that this CO_2^- anion radical surrounded by potassium ions has limited thermal stability (which is in agreement with its established properties (*7, 13, 20–23*)), and it may transform into more stable surface species. This structural rearrangement is exhibited by a shift of band positions from 1695 to 1675 cm^{-1} and from 1325 to 1365–1375 cm^{-1}, and by the production of a new band at 1525 cm^{-1}. On the basis of the above consideration, one could attribute these bands to bidentate carbonate species coordinated to K^+ ions. However, the new pair of bands at 1675 and 1365 cm^{-1} exhibits much less stability than bidentate carbonates; i.e., it disappears after evacuation at 300 K (Fig. 3). Therefore, we prefer an alternative explanation, namely a change in the coordination and stoichiometry of the K^+–CO_2^- surface complex in this temperature range (for instance the transformation of monodentate to bidentate; see structure A and B in Fig. 7) which could also result in a shift to lower frequency (*18, 20, 21*). The formation of bidentate carbonate on this sample is characterized by stable bands at 1660, 1525, and 1360 cm^{-1}; the first one is clearly observed after elimination of previous bands in this region:

$$CO_{2(g)} \xrightarrow{<170\ K} CO^{-}_{2(a)}[\text{monodentate}] \xrightarrow{170\text{–}300\ K} CO^{-}_{2(a)}[\text{bidentate}].$$

Similar features were observed for the Rh-free sample with the exception that the pairs of bands exhibited higher thermal stabilities and a band at 1420 cm^{-1} instead of at 1525 cm^{-1} appeared.

It is an interesting characteristic of the interaction of CO_2 with K-modified samples that it does not produce CO in detectable amounts. This is in contrast to the behavior observed for Rh(111) and Pd(100) surfaces when potassium adatoms induced the dissociation of CO_2 even below room temperature (*7, 13, 22*). A possible reason is the fact that in the present case the activation of CO_2 occurs on highly dispersed silica-supported Rh, where the metal–potassium contact, which is presumably required for CO_2 dissociation to occur, may be reduced or even prevented. Alternatively, the dissociation may have taken place but the CO formed desorbed into the gas phase and escaped detection.

4.4. *Reaction of Adsorbed CO_2 with Hydrogen*

In the presence of hydrogen new spectral features (absorptions at 1600 and 1360 cm^{-1}) appeared, indicating a surface reaction and the production of new surface species. These bands were produced already at 150–160 K and grew in intensity up to 270 K. The bands are characteristic of adsorbed formate species: the 1600- and 1360-cm^{-1} bands are very probably due to the antisymmetric and symmetric O–C–O stretching vibrations, and the weak band at 2810 cm^{-1} is due to the C–H stretching vibration. Control measurements with HCOOH adsorption resulted in a similar spectrum.

Before the interpretation of these results it should be emphasized that formate species have not been identified on Rh/SiO$_2$ either by co-adsorption of $H_2 + CO_2$ or by direct HCOOH adsorption at 300 K (*9, 38*). The reasons are that formate species do not exist on pure silica (*39, 40*) and they are not stable on a K-free Rh above 250 K (*9, 41, 42*). The formation of formate species was, however, promoted on a K-modified Os/Al$_2$O$_3$ catalyst following CO adsorption at higher temperatures due to conversion of HCO_3^- and CO_3^{2-} species with hydrogen (*43*).

In the production of formate species in the present case the potassium additive can play the following roles: (i) activation of CO_2 by electron donation, (ii) stabilization of carbonate-like species on the silica in the form of a potassium salt, and (iii) stabilization of formate species on Rh or silica in the form of potassium formate (*42*).

Let us examine the importance of these points separately. There is no doubt that the easiest way to form formate is the reaction

$$CO^{-}_{2(a)} + H_{(a)} \rightarrow HCO^{-}_{2(a)}.$$

This step is particularly important at low temperatures when CO_2^- exists on the surface. As the formate species was also produced in the reaction of surface carbonate and hydrogen (Fig. 5), the stabilization of this carbonate species and its reaction with hydrogen seems to represent the major route in the formation of formate at higher temperature. The stabilization of formate by potassium seems also important as otherwise it could not accumulate on the Rh/SiO$_2$ sample at 300 K (*9, 41, 42*).

Whereas the $H_2 + CO_2$ co-adsorption on Rh/SiO$_2$ produced CO even at 255 K, as indicated by the adsorption bands at 2045 and 2015 cm^{-1} (Fig. 1), this was not observed in the presence of potassium even at higher temperatures. In contrast, a broad spectral feature appeared at 1720–1760 cm^{-1} which was not accompanied by new absorptions at 1200–1400 cm^{-1}. The 1720- to 1760-cm^{-1} band vanished only above 423 K (Fig. 5B). A possible candidate for the assignment of this band is a bicarbonate species. However, the antisymmetric stretch of both monomeric and dimeric species lies below 1700 cm^{-1} (*18*). The high frequency of the observed band and the absence of the symmetric stretch therefore render this assignment unlikely. We may consider the formation of bridge-bonded carbonate, which has a strong absorption at 1700–1780 cm^{-1} (antisymm.) and a large $\Delta\nu_3$ splitting (400 cm^{-1} or higher) (*18*). However, the symmetric stretch is again missing and it would be difficult to explain why hydrogen is needed for the formation of this species. The most probable explanation is that the 1720- to 1760-cm^{-1} band belongs to bridge-bonded CO on Rh crystallites which was very probably produced in the decomposition of surface formate species. In the case of K-free samples, bridge-bonded CO gives an absorption band at higher frequency, namely at ~1860 cm^{-1}, which indicates that in the present case the potassium led to a significant shift of the absorption band of CO to lower frequencies. However, when CO was adsorbed on this sample no appreciable shift of the bridging CO bands was observed. This is in agreement with the results reported by Blackmond *et al.* (*44*), who detected only a very small shift of linearly and bridge-bonded CO on Cs-modified Rh/Al_2O_3. Despite such minute effects on the carbonyl spectra, alkali additives strongly affected the rate and product distribution of the hydrogenation of CO (*44, 45*) and of CO_2 (*46*) on Rh catalysts. This suggests that the number of alkali-modified Rh sites (which may be considered the most active sites in the hydrogenation reactions) is markedly lower than the number of Rh sites capable of adsorbing CO molecules. It should be noted that potassium adatoms exert a much more drastic effect on transition metal single-crystal surfaces (the "red" shift of CO bands was reported to be 470–640 cm^{-1} (*47*)).

Although most of the surface species detected appear to reside on K^+-sites on the silica support or at the metal/support interface, it is important to point out that no formate was produced on potassium-promoted samples in the absence of rhodium (Fig. 6). In this case, the spectral feature observed at 1720–1760 cm^{-1} for the Rh-containing sample was also absent. This clearly indicates the importance of Rh in the formation of formate and in subsequent reactions. The possible role of the Rh is to produce activated hydrogen, which by migrating from the Rh surface to the silica or to the interface, reacts with carbonate species.

5. CONCLUSIONS

1. Adsorption of CO_2 was found to be weak and molecular on Rh/SiO_2 at temperatures below 300 K.

2. Preadsorbed potassium increases the binding energy of CO_2 and leads to the formation of CO_2^- anion species above 130 K. Electron donation is attributed to K_2O. It is proposed that the CO_2^- ion is bonded to the K^+ ion on both $(K + Rh)/SiO_2$ and K/SiO_2. Depending on its coordination and structure this surface species is characterized by different pairs of absorption bands.

3. Above 280 K, the K^+–CO_2^- surface complex is transformed into a more stable bidentate carbonate coordinated to K^+ ions.

4. CO_2^- reacts with hydrogen on K-modified Rh/SiO_2 at temperatures as low as 150 K to give formate species which are stabilized in the form of a potassium salt. Reaction of bidentate carbonate with hydrogen also yields surface formate.

5. No formate was produced on Rh-free K/SiO_2 surfaces.

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