JOURNAL OF CATALYSIS 65, 428–436 (1980)

Surface Interaction between H_2 and CO_2 on Rh/Al_2O_3, Studied by Adsorption and Infrared Spectroscopic Measurements

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Received January 9, 1980; revised April 14, 1980

The low-temperature interaction between $H_2 + CO_2$ on Rh/Al_2O_3 was investigated by adsorption and infrared spectroscopic measurements. Adsorption studies indicated that the presence of H_2 greatly enhances the uptake of CO_2 by Rh/Al_2O_3 catalyst. Infrared spectroscopic studies revealed that adsorbed formate and CO are formed in the low-temperature interaction between H_2 and CO_2. On comparison of the spectrum of adsorbed CO with that obtained after coadsorption of the H_2 + CO_2 mixture, it appeared that (i) the doublet due to twin CO ($Rh/CO/_2$) was completely missing, (ii) the linearly bonded CO appeared at lower frequency, 2020–2039 cm^{-1}, and (iii) no significant change was observed in the position of the bridged CO. The apparent activation energy of the formation of formate ion was calculated to be 4.2 kcal/mol, which is markedly lower than that determined for pure Al_2O_3, indicating the great promoting effect of Rh. Possible mechanisms of the $H_2 + CO_2$ interaction are discussed.

INTRODUCTION

Rhodium is a very effective catalyst for hydrogenation of CO_2 to CH_4 (*1, 2*). The rate per unit surface area of Rh is considerably higher than that for hydrogenation of CO either on polycrystalline Rh (*1*) or on alumina-supported Rh (*2*). The value of the activation energy, 16 kcal/mol, is also lower for CH_4 formation from a $H_2 + CO_2$ mixture than from a H_2 + CO mixture. These results suggest that the most important elementary steps in CH_4 formation, the reaction of surface intermediates, occur favorably when CO_2 is used as a reactant. In order to obtain a deeper insight into the nature of the $H_2 + CO_2$ reaction, in the present work the surface interaction between H_2 and CO_2 has been investigated by adsorption and infrared spectroscopic measurements on the same Rh/Al_2O_3 sample as used in the catalytic studies (*2*).

EXPERIMENTAL

Materials. The catalysts were prepared by impregnating an alumina support (Degussa P 110 Cl) with a solution of $RhCl_3 \cdot 3H_2O$ to yield a nominal 5 wt% metal. The impregnated powders were dried at 393 K. For catalytic and adsorption measurements, small fragments of slightly compressed pellets were used. For infrared studies, transparent thin 30 × 10-mm wafers were prepared at high pressures (1600 atm). The sample thickness varied in the range 15–20 mg/cm^2. Before any measurements, the catalyst was oxidized with 100 Torr O_2 for 30 min and reduced with 100 Torr H_2 for 30 min at 673 K *in situ*. After oxidation and reduction, the sample was evacuated prior to adsorption and infrared spectroscopic measurements or flushed with pure N_2 for pulse experiments at 673 K. The dispersity of Rh was 30.2%.

The gases used were initially of commercial purity. They were purified by fractional distillation (CO_2) or by adsorbing the impurities at the temperature of liquid air using a molecular sieve. The purities of the gases were checked by mass spectrometry.

Methods. Adsorption measurements were made in a Sartorius microbalance. Infrared spectra were recorded by a Specord 75 IR double-beam spectrometer (Zeiss, Jena). The instrument scans the region from 4000 to 400 cm^{-1} at a rate of

0021-9517/80/100428-09$02.00/0

from 0.1 to 27 wavenumbers/sec. In order to enhance the sensitivity, an appropriate attenuator was used in the reference light path. The resolution was better than ±5 cm^{-1}. The apparatus was calibrated with 0.02-mm-thick polystyrene foil and also with a gas cell containing CO at 150 Torr.

A Kiselev-type infrared cell was used with NaCl windows. A detailed description of the cell has been given elsewhere (*3*). The cell was connected to a traditional gas-handling and vacuum system. All spectra were recorded at the temperature of the infrared beam, about 313 K.

The dispersity of the supported Rh was determined by H_2 adsorption at 298 K and atmospheric pressure using dynamic impulse methods (*4*, *5*). The H_2 uptake was 73 μmol/g.

RESULTS AND DISCUSSION

Adsorption Studies

The adsorption of CO_2 on Rh/Al_2O_3 begins as a very fast process, the extent of which decreases with increase of the adsorption temperature (Fig. 1). This fast adsorption is followed by very slow adsorption of CO_2. About 30–50% of the adsorbed CO_2 can be pumped off at the temperature of adsorption. Almost the same gas uptakes were registered on the Al_2O_3 support alone, which may indicate that CO_2 does not chemisorb on Rh, or at least that its adsorption is very limited.

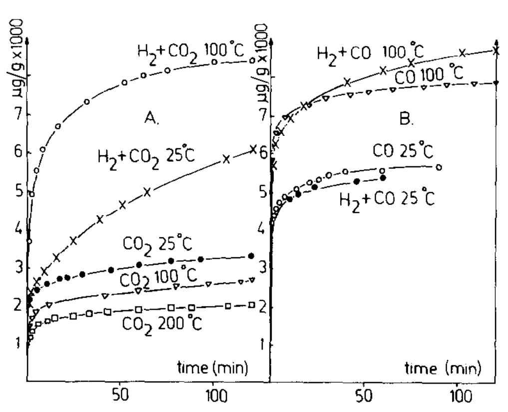


FIG. 1. Adsorption of 20 Torr CO_2 and 40 Torr H_2 + CO_2 (1 : 1) (A), and 20 Torr CO and 40 Torr H_2 + CO (1 : 1) (B) on reduced Rh/Al_2O_3 at different temperatures.

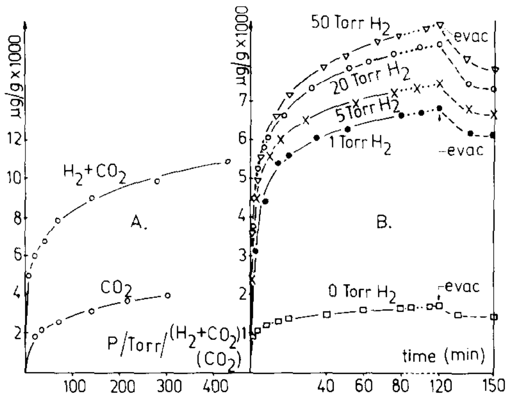


FIG. 2. (A) Adsorption isotherms of CO_2 and H_2 + CO_2 (1 : 1) on Rh/Al_2O_3 at 373 K. (B) The effect of amount of H_2 on the gas uptake from the H_2 + CO_2 mixture on Rh/Al_2O_3 at 373 K. The pressure of CO_2 was 20 Torr.

In contrast, as Fig. 1 shows, CO adsorbs strongly and to a greater extent on Rh. On Al_2O_3 the adsorption of CO is much less than that of CO_2. As regards the adsorption of H_2, we refer to the determination of dispersity of Rh by H_2 chemisorption.

In subsequent measurements the coadsorption of H_2 + CO_2 (1 : 1) was investigated. The uptake from this gas mixture was markedly larger than the sum of the separately adsorbed gases (Fig. 1). With an increase in the pressure of the H_2 + CO_2 mixture, the amount of gas uptake greatly increased (Fig. 2). Approximate saturation was reached at 600 Torr. In this case the amount of strongly held adsorbed gases that remaining after 30 min evacuation at 373 K was 9.38 mg/g catalyst. Under similar conditions 2.27 mg CO_2 remained adsorbed on 1 g catalyst. (No such phenomenon occurred on alumina in the absence of Rh.) In contrast to the adsorption of CO_2, on evacuation at 298 or 373 K only 10–15% of the adsorbed gases was desorbed and the extent of gas uptake from the H_2 + CO_2 mixture increased with the temperature up to 303 K.

From further experiments it appeared that the addition of even 1 Torr H_2 to the

CO_2 greatly enhanced the amount of gas adsorbed. After increasing of the pressure of H_2, the extent of gas uptake increased further (Fig. 2).

When H_2 was preadsorbed at 298 or 373 K for a given time, and the gaseous and weakly adsorbed H_2 was then evacuated, an appreciable increase of subsequent CO_2 adsorption was also experienced. The extent of enhanced CO_2 adsorption increased with the amount of chemisorbed H_2, but it was always less than the value obtained during the coadsorption measurements.

A possible reason for the enhanced adsorption from the $H_2 + CO_2$ mixture is that adsorbed hydrogen reacts with CO_2, producing CO

$$2H_{(a)} + CO_2 = CO_{(a)} + H_2O_{(a)} \qquad (1)$$

which, as Fig. 1 shows, adsorbs on Rh to a greater extent than does CO_2. In harmony with this assumption, preadsorbed CO markedly decreased the extent of the enhanced adsorption from the $H_2 + CO_2$ mixture (Fig. 3). On the other hand, when the $H_2 + CO_2$ gas mixture was adsorbed on Rh/Al_2O_3 for 60 min at 298 K, practically no significant change occurred in the subsequent adsorption of CO. After adsorption of the $H_2 + CO_2$ mixture at 373 K, however, when an enhanced gas uptake occurred, the extent of subsequent adsorption of CO at 298 K was greatly reduced (Fig. 3).

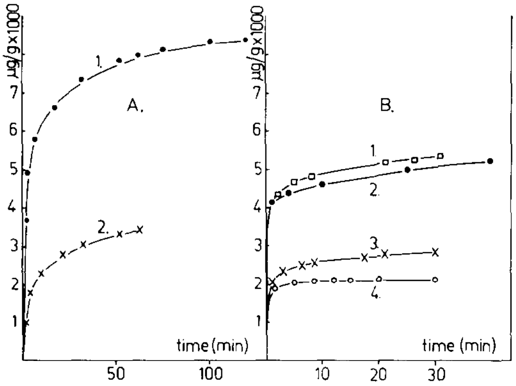


FIG. 3. (A) Adsorption of 40 Torr $H_2 + CO_2$ (1 : 1) at 373 K (1) on reduced Rh/Al_2O_3, and (2) on the sample saturated with CO at 298 K. (B) Adsorption of CO at 298 K (1) on reduced Rh/Al_2O_3, (2) on samples treated with 40 Torr $H_2 + CO_2$ (1 : 1) for 60 min at 298 K, (3) for 60 min at 373 K, and (4) on the sample saturated with $H_2 + CO_2$ (1 : 1) at 373 K.

As mass-spectrometric analysis of the gas phase during the coadsorption of $H_2 + CO_2$ at 298–373 K did not reveal any reaction; we had to assume that all the products of the water–gas shift reaction remained adsorbed on the Rh/Al_2O_3 surface.

Assuming that the CO formed in the above reaction is adsorbed on the Rh and that the water is adsorbed on the alumina, from the amount of gas uptake from the $H_2 + CO_2$ mixture (at saturation and at 373 K) we determined that 148 μmol CO/g and 148 μmol H_2O/g are formed in the surface reaction.

The maximum uptake of CO by the Rh of this sample under more favorable conditions (at 373 K and at 600 Torr CO), however, was 165 μmol/g, which is only slightly higher than the above value.

In the interpretation of this result, one can assume that the adsorbed hydrogen promotes the adsorption of CO. As one Rh atom is capable of adsorbing two CO molecules, it can also be assumed that the formation of this surface species is more favorable in the presence of H_2. The results presented in Fig. 1, however, show that this is not the case, for practically the same gas uptake was obtained from the H_2 + CO mixture as from CO alone, and, as will be shown later, the *adsorbed hydrogen hinders the formation of the twin structure of adsorbed CO.*

Accordingly, it seems more likely that, in addition to the formation of CO and H_2O, the surface interaction between H_2 and CO_2 on Rh/Al_2O_3 produces a surface complex which also contributes to the increased gas uptake.

In order to obtain a deeper insight into the surface processes during the coadsorption of the $H_2 + CO_2$ mixture, infrared spectroscopic measurements were carried out.

Infrared Spectroscopic Measurements

Adsorption of CO_2 at 25 Torr on reduced 5 wt% Rh/Al_2O_3 at 298–373 K produced bands at 1625–1640, 1436, and 1230 cm^{-1} (Fig. 4), which can be attributed to the formation of carbonate species. The intensities of these bands showed a very slight variation with adsorption time and temperature. Similar experiments on alumina resulted in the same infrared spectra.

No bands due to adsorbed CO, indicative of the dissociation of CO_2, were observed in the spectra *at this pressure*. This result, in harmony with the observations of previous workers on Rh films (*6*), on polycrystalline Rh (*7*), and on alumina-supported Rh (*8*), shows that the adsorption of CO_2 on Rh is very weak. In contrast, however, Somorjai *et al.* (*9, 10*) found that CO_2 does chemisorb and dissociate on several faces of Rh single crystals.

From our more detailed investigations concerning this question, we found that the dissociation of CO_2 occurs to a small extent on supported Rh, too. The preparation of the catalyst, the dispersity of the Rh, and the nature of the support all have an influence on this process. On the sample used in the present work, weak bands due to CO, indicating the occurrence of dissociation of CO_2, appeared at 373 K when a high pressure (200 Torr) of CO_2 was used.

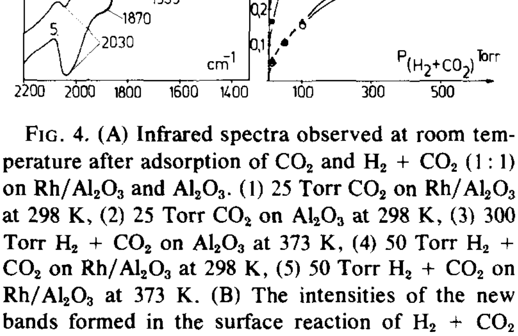


FIG. 4. (A) Infrared spectra observed at room temperature after adsorption of CO_2 and $H_2 + CO_2$ (1 : 1) on Rh/Al_2O_3 and Al_2O_3. (1) 25 Torr CO_2 on Rh/Al_2O_3 at 298 K, (2) 25 Torr CO_2 on Al_2O_3 at 298 K, (3) 300 Torr $H_2 + CO_2$ on Al_2O_3 at 373 K, (4) 50 Torr $H_2 + CO_2$ on Rh/Al_2O_3 at 298 K, (5) 50 Torr $H_2 + CO_2$ on Rh/Al_2O_3 at 373 K. (B) The intensities of the new bands formed in the surface reaction of $H_2 + CO_2$ (1 : 1) on Rh/Al_2O_3 at 373 K as a function of $H_2 + CO_2$ (1 : 1) pressure. The points correspond to the stage when the intensities of the bands approached a steady value.

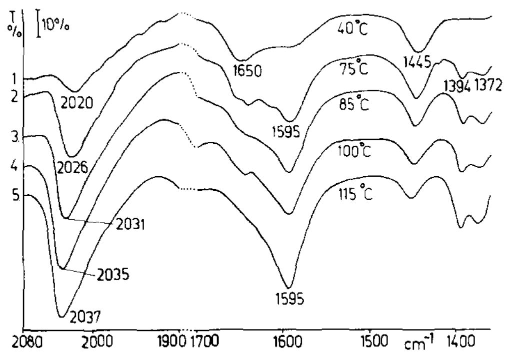


FIG. 5. Infrared spectra observed at room temperature after adsorption of 40 Torr $H_2 + CO_2$ (1 : 1) on Rh/Al_2O_3 at different temperatures for 5 min. The cell was evacuated at the adsorption temperature before the registration of the spectra.

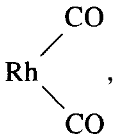
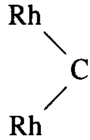
Adsorption of H_2 on supported Rh at 298–673 K produced no detectable absorption bands in the frequency range 1000–4000 cm^{-1}, in agreement with the observation of Yates *et al.* (*11*).

Upon admitting the $H_2 + CO_2$ mixture (25 Torr of each gas) into the cell at 298–373 K, the following spectral changes occurred. Even at the beginning of the adsorption, new bands appeared between 2020 and 2039 and at 1870 cm^{-1} (Fig. 4). In addition, new bands were also identified in the low-frequency region, at 1595, 1393, and 1375 cm^{-1}, and a very weak one at 2914 cm^{-1}. Their intensities slowly grew in time and with the pressure of $H_2 + CO_2$ (Fig. 4). On raising the adsorption temperature, the intensity of the band between 2020 and 2039 cm^{-1} increased up to 388 K, but it decreased above this temperature. In contrast, the intensities of the other new bands grew with the increase of the adsorption temperature up to 573 K. At the same time the intensities of the bands due to surface carbonate gradually decreased (Fig. 5).

It is to be mentioned that these bands

were not detected on pure alumina under the same conditions. They appeared, however, when the H_2 + CO_2 mixture (300 Torr) was adsorbed on alumina at the higher temperatures of 473–673 K and then evacuated at 298 K.

In order to facilitate the interpretation of the above results, we examined the infrared spectra of adsorbed CO and HCOOH, recorded under the same conditions.

Infrared spectroscopic measurements on the adsorption of CO over Rh/Al_2O_3 unequivocally show that three kinds of adsorbed CO exist on the surface (*12–21*): a twin structure,  $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{CO}}{\diagdown \mathrm{CO}}$, absorbing at 2101 and 2035 cm^{-1}; a linear form, Rh—CO, absorbing at 2060–2070 cm^{-1}; and a bridged form,  $\genfrac{}{}{0pt}{}{\mathrm{Rh}\diagdown}{\mathrm{Rh}\diagup}\mathrm{CO}$, yielding a broad band at 1855–1870 cm^{-1}. The most interesting feature of the adsorption of CO is the formation of the twin structure. It is now generally believed that the high dispersity of the Rh favors the formation of this species. In the further details, however, opinions differ.

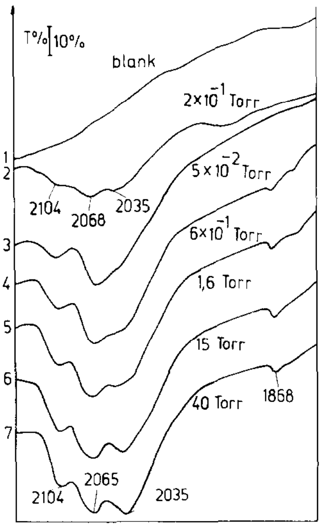


FIG. 6. Infrared spectra observed at room temperature after adsorption of CO of different pressure on Rh/Al_2O_3 at H 298 (spectrum 2) and 373 K (spectra 3–7).

While French workers (*16, 17*) assign its formation to Rh(I) formed during the dissociation of CO on Rh, Yates *et al.* (*19*) assume that this species forms on atomically dispersed Rh atoms. Yates *et al.* (*20*) attribute its formation to the edge or corner atoms of two-dimensional rafts of Rh atoms.

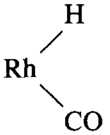
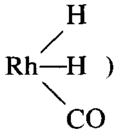
As the spectra in Fig. 6 show, the above surface species were formed on our sample (5 wt% Rh/Al_2O_3) too. The doublet due to the twin structure appeared at 2104 and 2035 cm^{-1}. Their intensities were almost equal. Weak bands due to bridged CO appeared at 1860–1870 cm^{-1}, and linearly bonded CO produced a band at 2060–2070 cm^{-1}. Its intensity increased with higher pressure and temperature.

On comparison of these spectra with that obtained after coadsorption of the H_2 + CO_2 mixture, the following can be stated about the latter spectrum:

(i) the doublet due to twin CO was completely missing;

(ii) the linearly bonded CO appeared at a somewhat lower frequency, 2020–2039 cm^{-1};

(iii) no significant change could be observed in the appearance of the bridged CO.

The absence of the twin structure cannot be attributed to the low surface concentration of CO, as the above surface structures appeared at all coverages of CO (Fig. 6). It is more probable that the adsorbed hydrogen prevents the formation of the twin structure, and that instead  $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{CO}}$ (or  $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{CO}}{-}\mathrm{H}$) is formed. The fact that the vibration of this species is somewhat lower than that of unperturbed linearly bonded CO is in agreement with the expectation that the H chemisorbed to the rhodium atom of a carbonyl is electron-donating, which increases the π-donation from the rhodium into the antibonding π orbital of the CO, resulting in a decrease in ν_{CO}. This shift in ν_{CO} was observed during the dissociative adsorption of H_2CO on highly dispersed Rh supported by alumina, when the twin band was also missing (*11*). It must be mentioned, however, that the admission of even 5.10^{-3}–10^{-1} Torr CO at 298 K onto a surface treated with the $H_2 + CO_2$ gas mixture at 573 K for 10 hr produced a twin band at 2104 and 2038 cm^{-1}. This may indicate that the CO formed in the $H_2 + CO_2$ surface reaction adsorbs on different sites, or in the presence of a larger amount of CO the adsorbed hydrogen will be replaced by CO. Analysis of the gas phase confirms this latter assumption.

Introduction of a very small amount of *HCOOH* gave very intense bands at 1585 and 1380 cm^{-1}, on either Rh/Al_2O_3 or Al_2O_3. A very weak band at 2914–2921 cm^{-1} was also identified. In agreement with previous workers (*22–25*), the 1585 and 1380 cm^{-1} bands are assigned to the asymmetric and symmetric O–C–O stretching vibrations of adsorbed formate ion. The weak band at 2914–2921 cm^{-1} is probably due to a CH stretching vibration. Above 373 K a weak band at 2030 cm^{-1} also appeared in the spectra (Rh/Al_2O_3, Fig. 7).

Comparison of these spectra with that obtained during the coadsorption of $H_2 + CO_2$ on Rh/Al_2O_3 permits the safe conclusion that formate groups are also formed in the $H_2 + CO_2$ interaction. The formation of formate bands in the surface interaction between H_2 and CO_2 was recently observed on Pd/Al_2O_3 (*26*) and on the other alumina-supported noble metals (*27, 28*). It was also detected in the $H_2 + CO$ reaction over Ru/Al_2O_3 (*29*) and on pure alumina, too (*25, 30*). As the formate group was identified on Rh/Al_2O_3 even at 298 K, while on the Al_2O_3 support it was detected only above 573 K, the favorable effect of Rh on the formation of formate is evident.

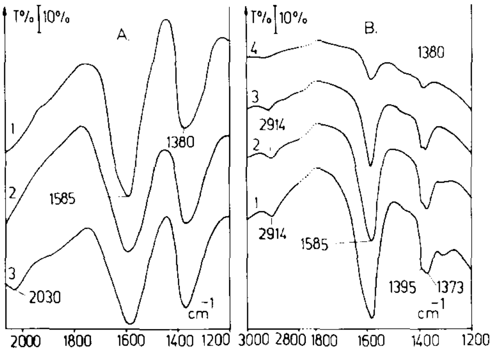
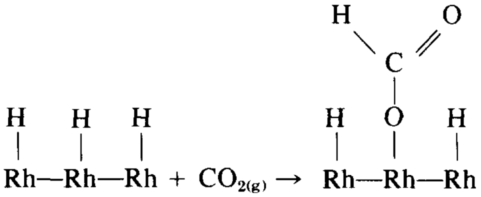


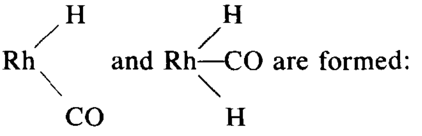
FIG. 7. Infrared spectra of adsorbed formic acid on Rh/Al_2O_3 (A) and Al_2O_3 (B). Temperatures and times of evacuation before registration of the spectra: (A) (1) 298 K for 30 min, (2) 373 K for 10 min, (3) 573 K for 10 min. (Amount of HCOOH introduced: 1.5×10^{-1} Torr.) (B) (1) 298 K for 30 min, (2) 473 K for 15 min, (3) 573 K for 15 min, (4) 673 K for 15 min. (Amount of HCOOH introduced: 6.5×10^{-2} Torr.)

The possible role of Rh is to activate the H_2 molecule. The adsorbed hydrogen atoms react with CO_2 yielding formate groups:

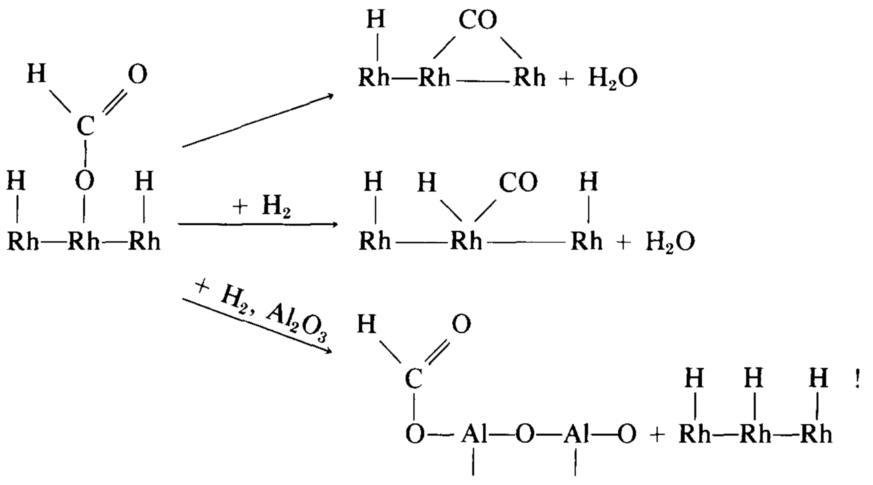


$$\underset{\mathrm{Rh}\text{—}\mathrm{Rh}\text{—}\mathrm{Rh}}{\mathrm{H}\quad\mathrm{H}\quad\mathrm{H}} + CO_{2(g)} \rightarrow \underset{\mathrm{Rh}\text{—}\mathrm{Rh}\text{—}\mathrm{Rh}}{\mathrm{H}\quad\overset{\overset{\mathrm{H}\diagdown\mathrm{C}\diagup\!\!\diagup\mathrm{O}}{|}}{\mathrm{O}}\quad\mathrm{H}} \qquad (2)$$

Taking into account the observations that CO is also formed and that the intensities of the bands due to formate ion increase in time and also with elevation of the temperature, we may assume that a part of the formate decomposes (reactions 3 and 4) on Rh and the remainder migrates from Rh onto the alumina support, on which it is much more stable (reaction 5). In the presence of a large excess of H_2, the twin structure cannot develop, and instead



$\mathrm{Rh}(\mathrm{H})(\mathrm{CO})$ and $\mathrm{H}\text{—}\mathrm{Rh}(\mathrm{H})\text{—}\mathrm{CO}$ are formed:



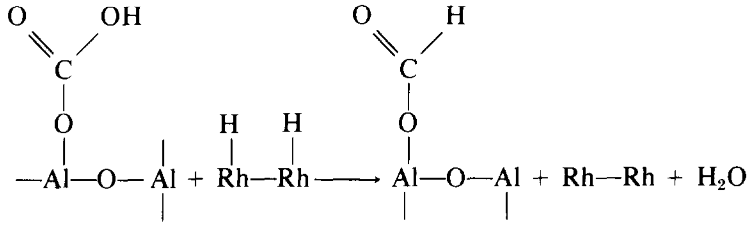
(3)

(4)

(5)

Control measurements showed that Rh can catalyze the decomposition of formic acid above 373 K, yielding CO, H_2O, H_2, and CO_2. On Al_2O_3, measurable decomposition was observed only above 473 K. It is very likely that the migration of formate from Rh onto alumina is a very fast process at 373 K, as there is no indication of the presence of rhodium formate in the spectra.

Although this explanation seems to be the most probable one, we cannot exclude the possibility that the formation of formate groups occurs on the alumina support. The hydrogen atoms formed in the dissociative adsorption on H_2 of Rh migrate to the adjacent acceptor sites on the alumina, in the present case the adsorbed CO_2, which is probably in the form of hydrocarbonate (*31*), producing surface formate group:



(6)

This formate group may diffuse farther, or, interacting with adjacent Rh atoms, decomposes into the products of Eqs. (2) and (3).

The following experiments show that this process can contribute, at least to a small extent, to the observed phenomena. When the Rh/Al_2O_3 surface was saturated with CO_2 at 298 K and, after a short evacuation at 10^{-3} Torr, 50 Torr H_2 was introduced, there was no indication of the formation of formate groups. This indicates that the migration of H atoms from Rh to alumina is very limited in this case. At 373 K, however, although the intensities of the carbonate species at 1630 and 1457 cm^{-1} after evacuation became one-third of those observed at 298 K, weak bands characteristic of the formate groups appeared in the spectra.

We may attempt now to calculate the amounts of formate formed in the low-temperature interaction of H_2 + CO_2. A correlation between the absorbance of the formate band at 1590 cm^{-1} and the amount of formate ion on the alumina was given by Amenomiya (*25*). Using his correlation, the surface concentration of formate ion formed at different temperatures was calculated from the absorbance of the band at 1590 cm^{-1}. In the determination of the surface concentration of formate ions the absorbances were calculated from transmittance results. It should be noted that no variation in the baseline was observed after pretreatment of the samples at 673 K. In order to eliminate the contribution of the formation of formate ion during the registration of the infrared spectra at about 313 K, the cell was evacuated after a certain time at the reaction temperature.

Assuming that the formation of formate ion occurs on Rh, the initial rate can be expressed in terms of the turnover number $N_{formate}$, the rate per unit surface area of the metal (Table 1).

From the temperature dependence of these values, the apparent activation energy of the formation of formate was obtained as 4.2 kcal/mol at 313–388 K. This is markedly lower than the value determined by Amenomiya on pure alumina at 473–573 K (20 kcal/mol), indicating that the Rh effectively promotes the formation of formate ion from the $H_2 + CO_2$ mixture.

The maximum amount of formate ion at 373 K is 266 μmol/g catalyst. As the surface area of the Al_2O_3 is 100 m^2/g, this means that the surface concentration of formate ion is 1.6×10^{14} ions/cm^2. This value is almost one order of magnitude larger than that obtained by Amenomiya (*30*) for pure Al_2O_3 at 573 K.

In conclusion, we can state the increased uptake of CO_2 by Rh/Al_2O_3 catalysts in the presence of H_2 can be attributed to the formation of formate ion, which is located on the alumina support. It has been shown that the low-temperature interaction of H_2 and CO_2 produces carbonylhydride species containing a single CO ligand and one or two H ligands.

TABLE 1

Formation of Surface Formate Ion at Different Temperatures[a]

Temperature (K)	Amount of formate ion formed in 5 min (μmol/g)	$N_{formate}$ ($\times 10^3$ sec^{-1})
313	34.82	0.79
333	68.55	1.55
348	76.27	1.73
358	94.28	2.14
373	99.76	2.27
388	148.31	3.37

[a] $N_{formate}$ = turnover number (molecules formed/metal site · sec). E = 4.2 ± 0.5 kcal/mol.

REFERENCES

1. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46,** 167 (1977).
2. Solymosi, F., and Erdöhelyi, A., *J. Mol. Catal.* **8,** 471 (1980).
3. Solymosi, F., Sárkány, J., and Schauer, A., *J. Catal.* **46,** 297 (1977).
4. Freel, J., *J. Catal.* **25,** 139 (1972).
5. Menon, P. G., Sieders, J., Streefkerk, F. J., and Van Keulen, G. J. M., *J. Catal.* **29,** 188 (1973).
6. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61,** 1504 (1957).
7. Campbell, C. T., and White, J. M., *J. Catal.* **54,** 289 (1978).
8. Collins, A. C., and Trapnell, B. M. W., *Trans. Faraday Soc.* **53,** 1436 (1957).
9. Castner, D. G., Sexton, B. A., and Somorjai, G. A., *Surface Sci.* **71,** 519 (1978).
10. Castner, D. G., and Somorjai, G. A., *Surface Sci.* **83,** 60 (1979).
11. Yates, J. T., Worley, S. D., Duncan, T. M., and Vaughan, R. W., *J. Chem. Phys.* **70,** 1225 (1979).
12. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69,** 1188 (1965).
13. Arai, H., and Tominaga, H., *J. Catal.* **43,** 131 (1976).
14. Yao, M. C., and Rothschild, W. G., *J. Chem. Phys.* **68,** 4774 (1978).
15. Solymosi, F., and Sárkány, J., *Appl. Surf. Sci.* **3,** 68 (1979).
16. Primet, M., *Trans. Faraday Soc. I* **74,** 2570 (1978).
17. Kaufherr, N., Primet, M., Dufaux, M., and Naccache, C., *C.R. Acad. Sci. Paris* **286,** 131 (1978).
18. Kroeker, R. M., Kaska, W. C., and Hansma, P. K., *J. Catal.* **57,** 72 (1979).
19. Yates, J. T., Duncan, T. M., Worley, S. D., and Vaughan, R. W., *J. Chem. Phys.* **70,** 1219 (1979).

20. Yates, D. J. C., Murrell, L. L., and Prestridge, E. B., *J. Catal.* **57,** 41 (1979).
21. Solymosi, F., Erdöhelyi, A., and Bánsági, T., submitted for publication.
22. Scholten, J. J. F., Mars, P., Menon, P. G., and Van Hardeveld, R., *Proc. Int. Congr. Catal., 3rd, 1964* **2,** 881 (1965).
23. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63,** 2300 (1967).
24. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
25. Amenomiya, Y., *Appl. Spectrosc.* **32,** 484 (1978).
26. Kadinov, G., Palazov, A., Shopov, D., Paper presented on the IV Intern. Congress in Varna 1979.
27. Erdöhelyi, A., Thesis, Szeged, 1977.
28. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *Trans. Faraday Soc. I.,* in press.
29. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **48,** 111 (1977).
30. Amenomiya, Y., *J. Catal.* **57,** 64 (1979).
31. Knözinger, H., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, P. B. Weisz, Eds.), Vol. 25, p. 184. Academic Press, New York, 1976.