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Surface Interaction between H_2 and CO_2 over Palladium on Various Supports

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The adsorption of CO_2 and its surface interaction with H_2 were investigated on Pd dispersed on SiO_2, MgO, TiO_2, and Al_2O_3 supports. No evidence was found for the dissociation of CO_2 at 300 K on any Pd samples. The occurrence of this process, however, was observed at 423 K. The adsorption measurements revealed that, with the exception of Pd/SiO_2, the presence of H_2 greatly enhances the uptake of CO_2 by Pd samples. The extent of the enhanced adsorption increased with rising temperature up to 423 K, and also with increase in the $H_2 + CO_2$ pressure. Infrared spectroscopic measurements showed that adsorbed CO and formate ion are formed in the surface interaction of $H_2 + CO_2$. The apparent activation energy for the formation of formate on Pd/Al_2O_3 was calculated to be 16.2 kJ/mol. On Pd/SiO_2 there was no enhanced adsorption, and only adsorbed CO was identified. No such phenomenon was observed in the absence of Pd, i.e., on the support alone. The development of the absorption bands due to the adsorbed CO formed differed from that observed following CO adsorption. It appeared that in the presence of hydrogen, Pd carbonyl-hydride is formed and the production of adsorbed CO in the surface reaction requires an ensemble of Pd atoms. It is concluded that the formate ion formed in the surface reaction is located on the support: the hydrogen activated on the Pd spills over onto the support and reacts with hydrocarbonate to yield formate ion.

INTRODUCTION

In a search for catalytic processes that may lead to the conversion of CO_2 to more valuable compounds, increasing attention is currently being paid to the catalytic chemistry of CO_2. As concerns the hydrogenation of CO_2, the results of earlier work are well documented in two reviews (*1, 2*), while new experiments data and conceptions can be found in papers (*3*).

The first deliberate attempts to determine the specific activities of methanation of CO_2 on metals (turnover frequencies, rates per unit metal surface area), and to compare them with the values measured for the methanation of CO, were made in our exploratory study (*4*). In that work we found that, among the Pt metals, alumina-supported Rh exhibited an outstanding catalytic performance in the methanation of CO_2 (*5*). For evaluation of its catalytic behavior, an extensive research program was undertaken, which involved studies of the surface interaction of $H_2 + CO_2$ below the temperature of the catalytic reaction (*5, 6*), the kinetics of hydrogenation of CO_2 (*7*) and CO (*8*), the dissociation of CO_2 (*5, 6, 9, 10*) and CO (*11, 12*), and the reactivities of surface carbon (*12*) and adsorbed formate (*6–8, 13, 14*) formed in the hydrogenation reactions. We deal with the main conclusions of these studies under Discussion and in our next paper.

We now apply the same complex approach to supported Pd, which is not very effective in methanation reactions, but which is quite active in CH_3OH synthesis from a gaseous $H_2 + CO$ mixture. The interaction of CO_2 with Pd and the hydrogenation of CO_2 on Pd catalysts have so far been the subject of only very few studies (*15–17*).

In this, the first of two papers, we examine the surface interaction of $H_2 + CO_2$ on Pd on four different supports at subme-

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thanation temperatures, while in the subsequent paper we report on the hydrogenation of CO_2 at higher temperatures with particular emphasis on the effects of the different supports.

EXPERIMENTAL

Materials. The catalysts were produced by incipient wetness impregnation of supports with $PdCl_2$ solution assumed to be H_2PdCl_4. This material was produced by dissolving $PdCl_2$ in concentrated HCl, and then evaporating the solution to dryness. The residue was dissolved in 1 *N* HCl. The Pd content of the catalyst was 1 or 5 wt%. After impregnation the sample was dried at 373 K. The following supports were used: Al_2O_3 (Degussa P110 Cl), SiO_2 (Aerosil 200), MgO (DAB 6), and TiO_2 (Degussa P25). Pd/SiO_2 was also prepared by a conventional ion-exchange method at 353 K using $Pd(NH_3)_2Cl_2$ solution. For adsorption measurements small fragments of slightly compressed pellets were used. For infrared studies, transparent thin 30 × 10-mm wafers were prepared at high pressures. The sample thickness varied in the range 15–20 mg/cm^2. Before any measurements the samples were decomposed *in situ* under vacuum at 673 K for 90 min, oxidized, reduced, and finally evacuated all at 673 K for 30 min.

In another preparation method, the dried powders were heated in H_2 up to 573 or 673 K with a heating rate of 40°/min and kept there for 60 min. The reduced samples were cooled to the temperature of the experiments under constant evacuation. This method resulted in a significantly higher dispersity of Pd. Characteristic data for the supported Pd samples are shown in Table 1.

The gases used were initially of commercial purity. They were carefully purified by fractional destillation (CO_2) or by adsorbing the impurities with a molecular sieve (Linde 5 Å) at the temperature of liquid air. They were deoxygenated with an "Oxy-Trap" and "Indicating Oxy-Trap" (Altech Co.).

TABLE 1

Some Characteristic Data of Supported Pd Catalysts

	Area of the supports (m^2 g^{-1})	Amount of Pd (wt%)	H/Pd	CO/Pd
Al_2O_3	100	5^a	0.042	0.071
(Degussa P 110 Cl)		5^b	0.19	0.23
		5^c	0.40	0.43
		1^a	0.044	—
TiO_2	150	5^a	—	—
(Degussa P 25)		1^a	0.04	—
SiO_2	240	5^a	0.096	0.095
(Aerosil 200)		1^a	—	0.27
MgO	170	5^a	0.096	0.095
(DAB 6)		1^a	—	0.1

[a] The sample was decomposed at 673 K under vacuum, then oxidized and reduced at 673 K for 30 min.

[b] The sample was heated in H_2 up to 673 K and kept there for 60 min.

[c] The sample was heated in H_2 up to 573 K and kept there for 60 min.

Methods. Adsorption measurements were performed in a Sartorius microbalance. Infrared spectra were recorded by a Specord 75 IR double-beam spectrometer (Zeiss, Jena). The instrument can scan the region from 4000 to 400 cm^{-1} at a rate from 0.1 to 27 wavenumbers/sec. The resolution was better than ±5 cm^{-1}. A Kiselev-type infrared cell was used with NaCl widows. A detailed description of the cell has been given elsewhere (*5, 6*). All spectra were recorded at the temperature of the infrared beam, about 313 K. The microbalance and the infrared cell were connected to a traditional gas-handling and vacuum system.

The dispersity of supported Pd was determined by $H_2 + O_2$ titration at 298 K, using the pulsed flow technique (*18*).

RESULTS

Adsorption Studies

The adsorption of CO_2 was first investigated on supported Pd catalysts. Some results are shown in Fig. 1. The adsorption of CO_2 began with a very fast process, the extent of which decreased with elevation of the temperature. The amount of adsorbed CO_2 was fairly high on Al_2O_3-, MgO-, and TiO_2-supported Pd, but it was very small on SiO_2-supported Pd. As practically the same gas uptakes were measured on the support alone as on the supported Pd samples, this

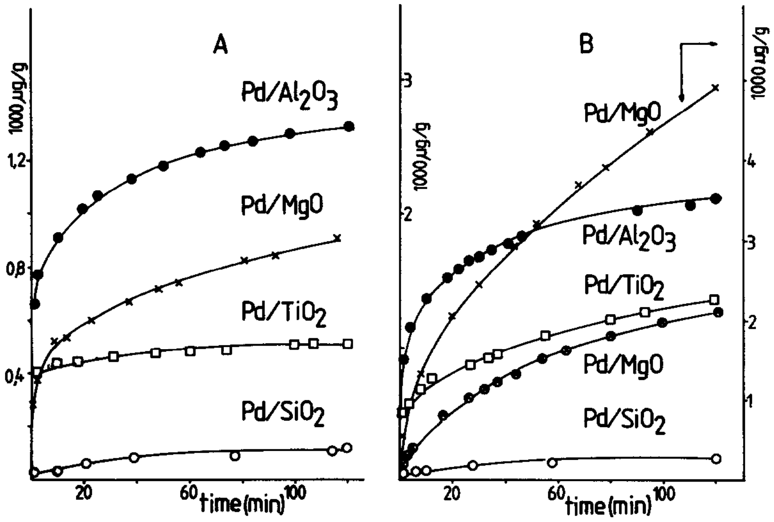


FIG. 1. (A) Adsorption of 20 Torr CO_2 and (B) $H_2 + CO_2$ (20 Torr each) on supported Pd samples at 373 K. The Pd content was 1 wt%. The effect of preadsorbed CO ($\theta \approx 1$) on the subsequent adsorption of $H_2 + CO_2$ is shown in the case of Pd/MgO (⊗).

feature made it almost impossible to establish the adsorption of CO_2 on the Pd and to determine its extent accurately and reliably. As CO_2 adsorbs weakly and reversibly on silica, the study of the adsorption of CO_2 on Pd/SiO_2 provided a possibility for investigation of this question. We found that, even with a 5% Pd/SiO_2 sample at 300 K, the adsorption of CO_2 remained reversible.

A completely different picture was obtained in the presence of hydrogen. Whereas no change in gas uptake was noted on the supports alone, on supported Pd (with the exception of Pd/SiO_2) there was considerably enhanced adsorption. Its extent decreases in the sequence Pd/MgO > Pd/Al_2O_3 > Pd/TiO_2 $\gg$ Pd/SiO_2. In the latter case, however, it was very small (Fig. 1B). This effect was observed even at 300 K; its extent increased with the rise of adsorption temperature up to 423 K and with the increase of the pressure of H_2. The enhanced adsorption also increased when the total pressure of the equimolar $H_2 + CO_2$ mixture was raised (Fig. 2). Approximate saturation was reached at 550–600 Torr.

In order to facilitate understanding of the reason for the enhanced adsorption from a $H_2 + CO_2$ mixture, the adsorption of CO (a possible product of surface interaction) was investigated on the same samples. From the CO adsorption isotherm extrapolated to zero CO pressure, the CO/Pd ratio was calculated. The data are collected in Table 1.

As the results plotted in Fig. 1B show, preadsorbed CO markedly decreased the extent of enhanced adsorption. On the other hand, when CO_2 or $H_2 + CO_2$ was preadsorbed on the 5% Pd/MgO surface at 473 K, the extent of subsequent adsorption of CO was greatly reduced.

Infrared Spectroscopic Measurements

To identify the surface species formed during the adsorption or surface interaction of $H_2 + CO_2$, detailed infrared spectroscopic measurements were carried out.

Pd/SiO$_2$. The adsorption of CO_2 at 300–423 K on 5% Pd/SiO_2 produced a band only at 2340 cm^{-1}, which disappeared during evacuation at 300 K. There was no indication of the appearance of any bands due to carbonate species or in the range of the CO stretching frequency at 300–473 K. On the sample with a higher Pd dispersity, ($D \approx$

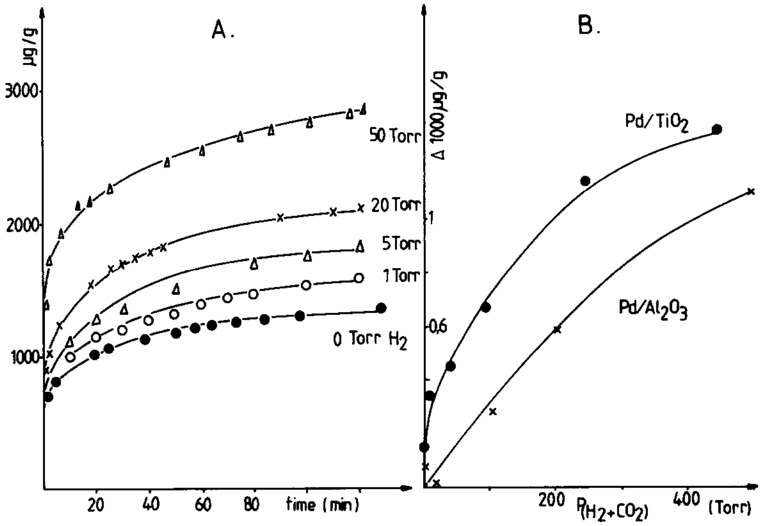


FIG. 2. (A) The effect of the amount of H_2 on the gas uptake from the $H_2 + CO_2$ mixture of 1% Pd/Al_2O_3 at 373 K. The pressure of CO_2 was 20 Torr. (B) Differences in the adsorption of $H_2 + CO_2$ (1 : 1) and CO_2 at 373 K on supported Pd samples as a function of pressure.

30%), a weak band at 1910 cm^{-1}, due to adsorbed CO, appeared at 423 K indicating the occurrence of the dissociation of CO_2.

The adsorption of $H_2 + CO_2$ on this sample at 300 K produced no new bands, even at high pressure (200 Torr each). At 423 K, however, a weak band appeared at 1900 cm^{-1}; its intensity increased slightly in time. At 473 K, another band was observed at 2070 cm^{-1} (Fig. 3). On exposure of this sample to CO at 300 K, a band first developed at 1960 cm^{-1}. At higher CO pressure, a very weak band was also detected at 2070 cm^{-1}. Admission of HCOOH produced an intense band at 1720 cm^{-1}, which was eliminated by evacuation.

Pd/MgO. The adsorption of CO_2 (20 Torr) on 5% Pd/MgO at 300 K produced carbonate bands at 1652, 1500, and 1410 cm^{-1} (Fig. 4). As the same absorption bands were observed following CO_2 adsorption on the MgO support alone (*6*), it seems that the presence of Pd does not exert a significant influence on the development of these carbonate bands, i.e., on the adsorption of CO_2 on MgO.

When the CO_2 adsorption was performed

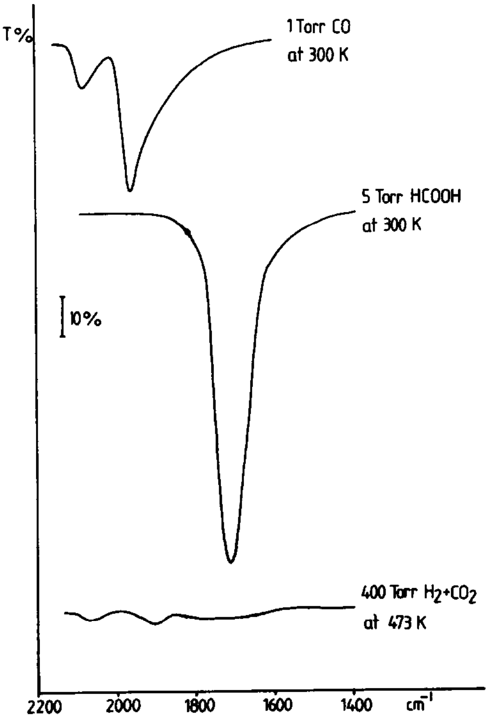


FIG. 3. Infrared spectra observed at room temperature following CO, $H_2 + CO_2$, and HCOOH adsorption on 5% Pd/SiO_2.

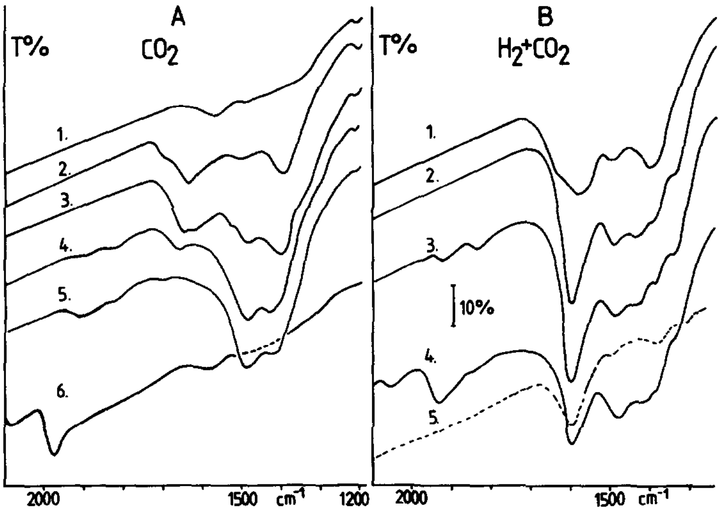


FIG. 4. Infrared spectra observed at room temperature following (A) CO_2 and CO, and (B) $H_2 + CO_2$ and HCOOH adsorption on 5% Pd/MgO. (A) (1) Background; (2) 300 K; (3) 373 K; (4) 423 K; (5) 473 K; (6) 1 Torr CO at 300 K. (B) (1) 300 K; (2) 373 K; (3) 423 K; (4) 473 K; (5) 1 Torr HCOOH at 300 K (---).

at higher temperature (423 K), weak bands due to adsorbed CO appeared at 1910 and 1820 cm^{-1}, indicating the occurrence of dissociation of the CO_2 on the Pd. Slight increases in the intensities of these bands were noted at higher temperatures.

More significant spectral changes took place *in the presence of* H_2 (adsorbing H_2 + CO_2 mixture, 20 Torr each). In addition to the carbonate bands, a strong band appeared at 1595 cm^{-1} and a weaker one at 1396 cm^{-1}, even at room temperature (Fig. 4). Their intensities increased with increase in pressure of the $H_2 + CO_2$ mixture, and also with the temperature and duration of the adsorption. They showed maximum intensity at 423 K. From the similarity of the IR spectrum of adsorbed HCOOH on Pd/MgO (Fig. 4), these bands can tentatively be attributed to adsorbed formate ion (*6*, *19*).

Absorption bands at 1935 and 1840 cm^{-1}, characteristic of chemisorbed CO, first appeared at 423 K, their intensities slightly increasing in time.

For the interpretation of the above IR spectra, we examined the adsorption of CO on this Pd/MgO sample. In the presence of CO (0.1 Torr) at 300 K, an intense band appeared at 1991 cm^{-1} and a weaker one at 2102 cm^{-1} (Fig. 4). With increase of the CO pressure, the latter band became more pronounced.

Pd/Al₂O₃. In this case, attention was also paid to the effect of the dispersity of the Pd. The adsorption of CO_2 on different Pd/Al_2O_3 samples at 300–473 K produced carbonate bands at 1642, 1458, and 1230 cm^{-1} (Fig. 5). Similar bands were observed on the alumina support alone. Spectral features at 1900 and 1810 cm^{-1}, characteristics of adsorbed CO, appeared first at 423 K. However, these bands were observed only in the IR spectrum relating to highly dispersed Pd ($D \approx$ 19–40%), and even in this case they were weak. Their intensities increased only very slightly when the temperature was raised further. Figure 5 also shows some spectra following CO adsorption.

In the presence of $H_2 + CO_2$ (20 Torr each), the formation of CO bands was greatly promoted. At the lowest temperature (373 K), bands appeared at 2070, 1918, and 1830 cm^{-1}. The intensities of these CO bands increased slightly in time, but more significantly when the sample temperature was elevated in the presence of the gas mix-

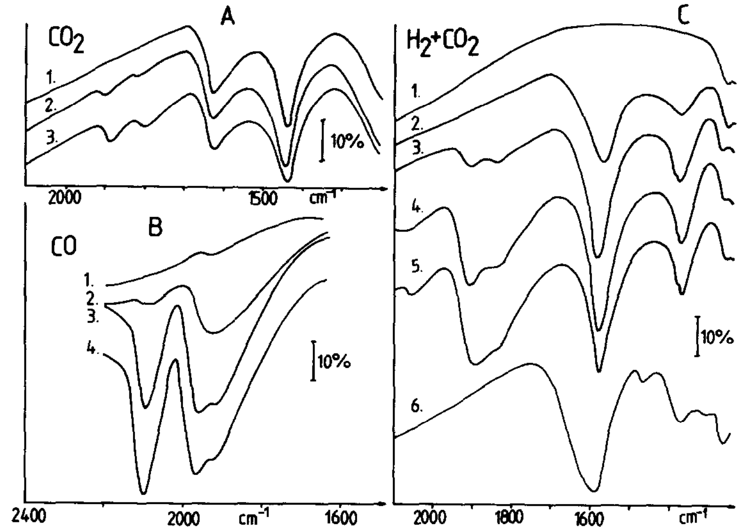


FIG. 5. Infrared spectra observed at room temperature following (A) CO_2 (20 Torr), (B) CO, (C) and $H_2 + CO_2$ (20 Torr each) adsorption on 5% Pd/Al_2O_3 (D = 40%). (A) (1) 373 K; (2) 423 K; (3) 473 K. (B) (1) 10^{-2} Torr; (2) 10^{-1} Torr; (3) 1 Torr; (4) 10 Torr. (C) (1) Background; (2) 300 K; (3) 373 K; (4) 423 K; (5) 473 K; (6) ~1 Torr HCOOH at 300 K.

ture. No appreciable shift occurred in the positions of these CO bands at higher intensities attained at 300–473 K (Fig. 5). At 423 K a weak band also developed at 2070 cm^{-1}. As concerns the effect of the Pd dispersity, it can be stated that the higher the dispersity of the Pd, the stronger the CO bands observed. In order to help the interpretation of these spectra, in Fig. 6 we displayed the effect of hydrogen on the IR spectrum of adsorbed CO. A slight downshift of the band at 1926 cm^{-1} occurred with the increase of the H_2 pressure.

The characteristic bands at 1595, 1396, and 1376 cm^{-1}, due to formate ion, were identified even at 300 K. Their presence was virtually independent of the dispersity of the Pd. The intensities of these bands increased with elevation of the temperature of adsorption up to 423 K and with increase in the pressure of the $H_2 + CO_2$ mixture (Fig. 6). In this case a weak band was also observed at 2920 cm^{-1}. It should be stressed that no formate species was detected on pure alumina, i.e., in the absence of Pd, under similar conditions below 573 K.

Pd/TiO₂. The transmittance of the reduced Pd/TiO_2 considerably deceased, which made the evaluation of the spectra difficult. The adsorption of CO_2 on Pd/TiO_2 at 300–423 K gave bands at 1640 and 1430 cm^{-1} which can be attributed to carbonate species formed on TiO_2. The intensities of these bands decreased with increase of the adsorption temperature. There was no indication for the dissociation of CO_2. When H_2 + CO_2 was adsorbed on Pd/TiO_2 the absorption band at 1580 cm^{-1} due to the formate species was clearly established. A very weak CO band also appeared at 1910 cm^{-1}.

DISCUSSION

Adsorption and Dissociation of CO_2 on Pd

In contrast to other simple gases, relatively little attention has so far been paid to the study of the interaction of CO_2 with clean transition metal surfaces. A noteworthy exception is Rh, on which detailed studies have been performed. Unfortunately, even in this case the results and theoretical calculations on the adsorption and dissocia-

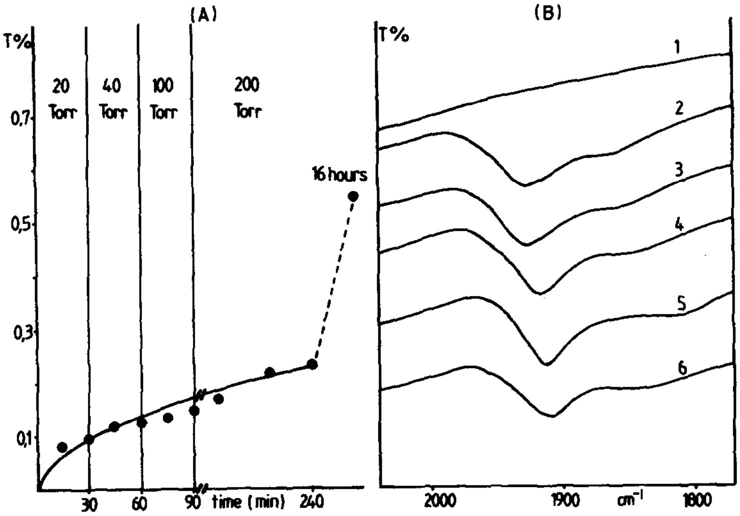


FIG. 6. (A) Changes in the intensities of the formate band at 1595 cm^{-1} formed in the surface interaction of $H_2 + CO_2$ on 1% Pd/Al_2O_3 at 373 K as a function of $H_2 + CO_2$ (1 : 1) pressure. (B) Effects of hydrogen on the infrared spectrum of adsorbed CO at lower coverage ($\theta \approx 0.2$) on 5% Pd/Al_2O_3 (D = 40%): (1) Background; (2) 10^{-2} Torr CO; (3) evacuation at 300 K; (4) $+5 \times 10^{-1}$ Torr H_2; (5) +1 Torr H_2; (6) +10 Torr H_2.

tion of CO_2 have proved quite contradictory (*20–23*).

Our recent measurements clearly showed that on a very carefully cleaned Rh(111) face and on Rh foil there is no adsorption and dissociation of CO_2 at low pressures (10^{-6} Torr) and at 300 K. However, boron, a common impurity in Rh, can induce the dissociation of CO_2 on Rh surfaces even below 300 K (*9, 10*).

As regards the reactivity of *clean* Pd surfaces toward CO_2 under UHV conditions, we have found no information in the literature.

Since CO_2 adsorbs easily and to a great extent on alumina, magnesia, and titania, it was practically impossible to make any conclusion concerning CO_2 adsorption on Pd from gravimetric measurements in these cases. The situation is more favorable for Pd/SiO_2, as CO_2 adsorbs only weakly on silica (*24, 25*). Even in this case, however, we found no evidence for the adsorption of CO_2 on the Pd surface. This conclusion is valid for both poorly dispersed and highly dispersed Pd samples. It is in contrast with the finding of Kadinov *et al.* (*15*), who assumed that the Pd surface is covered with adsorbed CO_2 at 300 K and stated that CO_2 dissociates on Pd even at this temperature. On our samples, absorption bands due to chemisorbed CO, indicative of the dissociation of CO_2, were detected from 423 K: weak bands appeared at 1900–1920 and 1810–1820 cm^{-1} (Figs. 3–5).

Taking into account the IR spectra of adsorbed CO on unsupported and supported Pd, and the assignments of the observed absorption bands (*26–30*, and references therein), we can conclude that the dissociation of CO_2 produces only multiply bonded CO. The band at 1900–1920 cm^{-1} relates to twofold coordinated CO, and the band at 1810–1820 cm^{-1} to threefold coordinated CO. In the temperature range 300–473 K and under the experimental conditions applied, there was practically no indication of the formation of linearly bonded CO absorbing around 2075 cm^{-1}. Accordingly, the dissociation of CO_2 very probably requires an ensemble of surface Pd atoms on which CO and O can remain bonded.

H_2 + CO_2 Coadsorption and Interaction

General features. Adsorption measurements revealed that the gas uptake from a 1 : 1 $H_2 + CO_2$ gas mixture onto supported Pd markedly exceeds the sum of the separately adsorbed gases. The enhanced adsorption was relatively small at room temperature, but its extent increased with rising temperature up to 423 K also with increase in the $H_2 + CO_2$ pressure. The attainment of saturation always required at least 550–600 Torr. Although enhanced adsorption was also observed on Pd/SiO_2, its extent was *significantly* less than on other supported Pd samples. As no such phenomenon was experienced on the support alone, we conclude that the Pd plays an important role in causing the enhanced adsorption.

A deeper insight into the nature of the surface interaction of $H_2 + CO_2$ was provided by IR spectroscopy. Several absorption bands appeared in the frequency region of the CO stretching vibration and, in addition, intense new bands developed at 1580–1600 and 1395 cm^{-1}. Since the same absorption bands were found following HCOOH adsorption on supported Pd samples and on the supports alone (Figs. 4 and 5), these bands can be attributed to the asymmetric and symmetric O—C—O stretching vibrations of formate ions. In certain cases, we could identify the C—H deformation of 1376–1350 cm^{-1}, and a band at 2915–2920 cm^{-1} relating to the CH stretching vibration.

Formation of adsorbed CO. Let us deal first with appearance of the CO bands in the $H_2 + CO_2$ surface interaction. One important observation is that in the presence of H_2, the CO bands were produced at lower temperatures and at higher intensities than in the absence of H_2. We believe that the CO is mainly formed as a result of the hydrogen-assisted dissociation of CO_2, but the decomposition of the formate at the Pd/support interface also contributes to its formation.

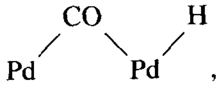
The IR spectrum of the CO frequency region, however, differed in several aspects from that following CO adsorption on the same samples. The main characteristics were as follows:

(i) the band at 1950–1970 cm^{-1} was shifted to lower frequency (Pd/Al_2O_3);

(ii) the band at 1800–1860 cm^{-1}, which did not appear in the IR spectra of our samples, or was very weak following CO adsorption, became more intense;

(iii) no or only a very slight shift occurred in the position of linearly bonded CO, and the intensity of this band remained extremely weak, even with the advance of the surface reaction.

From these results we may conclude that here, too, the formation of adsorbed CO requires an ensemble of Pd atoms. The fact that the CO bands appeared at somewhat lower frequencies, *even at higher intensities,* suggests that in the presence of a large amount of H_2, Pd carbonyl-hydride,



is formed.

Taking into account that the direction of the shift, we have to assume that the H chemisorbed on Pd is electron-donating, which increased the π-donation from the Pd into the antibonding π-orbital of the CO. (An alternative explanation involves the geometric effect; i.e., the hydrogen uncouples the dipole–dipole interaction which in turn leads to a decrease of the Pd–CO IR adsorption band.)

These results are in harmony with the finding of Vannice *et al.*, (*28*) who observed a downshift of 3–25 cm^{-1} in the high-frequency band (linear form) and a downshift of 0–40 cm^{-1} in the low-frequency band (twofold coordination) in the presence of H_2. We also experienced a downshift of ~16 cm^{-1} in the position of the 1926-cm^{-1} band when H_2 was admitted onto chemisorbed CO on Pd/Al_2O_3 ($D \approx 40\%$) at 300 K (Fig. 6).

In contrast, Palazov *et al.* (*29*) found that on Pd/Al_2O_3 the CO bands at 1915 cm^{-1} were shifted to higher frequencies after exposure of the surface to H_2, which was explained by the formation of an electronegative β-hydrogen coadsorbed with CO on the Pd surface. At the moment, we cannot explain these different behaviors. It cannot be excluded that two types of chemisorbed hydrogen exist on the Pd surface; the samples preparation, particle sizes, and nature of the support could all influence their formation and relative importance. It should be kept in mind that the experimental conditions under which adsorbed CO is formed are different in the present study, as CO produced in a surface reaction (which may involve surface sites different from those in the adsorption of CO) and in the presence of gaseous and chemisorbed hydrogen. The shift of the CO band to lower frequency occurs on other alumina-supported Pt metals (*5, 6, 31*), a feature which appears to be a general one for adsorbed CO formed in a surface reaction involving hydrogen.

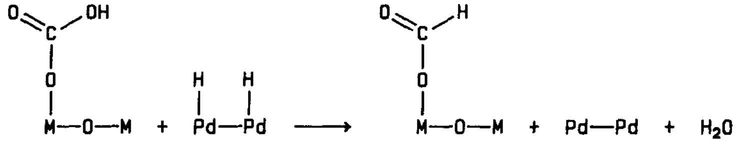
Formation and location of formate species. Although the formation of formate species on the $H_2 + CO_2$ surface interaction was clearly established, the nondependence of the formate bands on the adsorbents means that it is not easy to decide unambiguously whether the formate is bonded to the Pd or only to the support. Our experience with the supported Rh catalyst (*5, 6, 13*), however, strongly suggests that most of the formate is located on the supports.

Bearing this assumption in mind, we calculated the concentration of surface formate (from the data presented in Fig. 6) formed in the coadsorption of $H_2 + CO_2$ on 1% Pd/Al_2O_3. This was based on the correlation between the integrated area of the formate absorption band (1580–1600 cm^{-1}) and the amount of adsorbed formate (*4, 5*). The maximum amount of formate ion at 373 K is 79 μmole/g catalyst. If we relate these values to the number of surface Pd atoms, we find that the number of surface formate groups greatly exceeds the number of surface Pd atoms (at saturation by a factor of 15). This result strongly supports the idea that—similarly as for supported Rh (*4–8, 13*) and Ru (*31*) catalysts—*the formate ion mainly resides on the support.*

However, due to the insensitivity of the positions of the formate bands to the nature of the adsorbents, we cannot absolutely rule out the possibility that a portion of the formate is bonded to the Pd. During the literature search, we found no convincing evidence of the existence of formate ion on supported Pt metals. Hirota *et al.* (*32*) write that formate ion ($HCOO^-$) is produced on, among others, Pd during the adsorption of formic acid. Unfortunately, however, the given references (*33, 34*) do not contain any data on this metal at all. References to the statement of Hirota *et al.* (*32*) are made both in a textbook (*35*) and in a review (*36*). We note here that the interaction of HCOOH with Pd single-crystal surfaces has not yet been studied.

The question of the existence of formate ion on Pd can be answered by careful examination of the IR spectra obtained following HCOOH adsorption on Pd/SiO_2. HCOOH is known to adsorb in molecular form on SiO_2 (*37, 38*), and to only a small extent, in contrast with the other supports used in the present work.

Our investigation of the adsorption of HCOOH on Pd/SiO_2 at 300–473 K revealed only the band at 1720 cm^{-1}, which was also observed using SiO_2 alone. This band can be attributed to HCOOH bonded molecularly on SiO_2; it can be almost completely eliminated by room temperature evacuation. No bands due to adsorbed formate ion were identified at 1580–1600 cm^{-1} in the temperature range 300–473 K at 10 Torr HCOOH pressure. However, weak bands due to chemisorbed CO were observed at 1930 and 2050 cm^{-1}; these were formed in the decomposition of formic acid or in that of a transient, undetected formate species on the Pd. (Evaluation of the decomposition of HCOOH over Pd is not a subject of the present study. On analogy with Rh (*14*),



(M= metal ion of the support.)

SCHEME 1

and Pt (*39*), it appears very likely that its decomposition occurs in part through the transient formation of surface formate on the Pd.)

Accordingly, IR spectroscopy provides no evidence of the existence of stable formate species on Pd about 300 K. This consideration supports our earlier conclusion that the formate ion detected in the surface interaction of $H_2 + CO_2$ on Pd/MgO, Pd/Al_2O_3, and Pd/TiO_2 is located exclusively on the oxidic supports.

In interpreting the occurrence of formate species on the support, we emphasize that no formate is produced in the $H_2 + CO_2$ interaction on the support alone, i.e., in the absence of metal at 300–473 K. From the temperature dependence of the initial rate, the apparent activation energy of formation was obtained as 16.2 kJ/mol for Pd/Al_2O_3. This value is considerably lower than that measured for pure Al_2O_3, where the formation of formate in the $H_2 + CO_2$ reaction above 473 K occurred with an activation energy of 83.7 kJ/mol (*40*). This clearly illustrates the dominant role of the metal in the formation of the formate species.

Accepting the idea that formate is an unstable species on Pd, we can probably exclude the possibility that formate is formed in a surface reaction of adsorbed H and gaseous CO_2 *on the Pd itself* and then migrates onto the acceptor sites of the support.

It appears more likely that the hydrogen activated on the Pd spills over onto the support and reacts with adsorbed (and activated) CO_2 in the form of hydrocarbonate or carbonate (Scheme 1).

In order to substantiate this mode of formate formation, H_2 was admitted onto a Pd/MgO sample (at 373 K) saturated with CO_2 and containing hydrocarbonate species. As a result, weak bands indicative of the formation of formate species appeared in the IR spectrum at 1600 cm^{-1}, with a simultaneous decrease in the intensities of the hydrocarbonate bands at 1650 cm^{-1}.

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