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## Catalytic Hydrogenation of CO<sub>2</sub> over Supported Palladium

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The hydrogenation of CO<sub>2</sub> over Pd supported by Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, and MgO has been investigated in a flow technique at 1 and at 9.5 atm. For comparison the hydrogenation of CO was examined under the same experimental conditions. Attention was focused on the identification of surface species formed during the reaction. The hydrogenation of CO<sub>2</sub> occurred at a measurable rate above 520 K. It appears that the dispersion of Pd plays a governing role in determining the direction of the H<sub>2</sub> + CO<sub>2</sub> reaction. On highly dispersed Pd, the main product of the reaction was methane at both pressures while on poorly dispersed Pd the reverse water–gas shift reaction (at 1 atm) or methanol formation (at 9.5 atm) occurred. *In situ* infrared spectroscopic measurements revealed that multiply bonded CO and formate species were present on the catalyst surface during the reaction at 1 atm. The formation of surface carbon was also detected. From the behavior of surface formate under different conditions it was inferred that it does not play a significant role in hydrocarbon synthesis on Pd catalysts. On the basis of the specific activities, Pd/TiO<sub>2</sub> proved to be the most effective catalyst for the hydrogenation of CO<sub>2</sub>. It is proposed that the important step in the methanation of CO<sub>2</sub> is the dissociation of adsorbed CO. With respect to the high activity of Pd/TiO<sub>2</sub>, it is assumed that an electronic interaction operates between TiO<sub>2</sub> and Pd, influencing the bonding and reactivity of chemisorbed species. As concerns methanol synthesis at 9.5 atm, the results obtained failed to support the idea that methanol is produced in a direct reaction of CO<sub>2</sub> and not through formation of CO and its consecutive hydrogenation. © 1986 Academic Press, Inc.

### INTRODUCTION

In a previous paper (1) we examined the surface interaction of H<sub>2</sub> + CO<sub>2</sub> on Pd supported by alumina, magnesia, titania, and silica at CO<sub>2</sub> submethanation temperatures, 300–473 K. In this paper we report the catalytic hydrogenation of CO<sub>2</sub> on the same Pd catalysts at atmospheric pressure and at 9.5 bar. Special attention is focused on the identification and role of the surface species formed during the reaction and on the effects of the supports.

The abundance of CO<sub>2</sub> as a one-carbon precursor has recently evoked interest in its catalytic transformation (2, 3). One possible pathway for transfer of the carbon of CO<sub>2</sub> is the catalytic hydrogenation of CO<sub>2</sub>. This reaction has received appreciable attention only in recent years, when the catalytic effects of the following metals were tested: Ru (4–9), Rh (10–14), Pt (4), Ir (4),

Os (15), Ni (16–22), Co (9), Fe (9, 23), and Mo (24).

In our exploratory study we found that, of the Pt metals, alumina-supported Pd exhibits the lowest activity in the methanation of CO<sub>2</sub> (4). On the other hand, Rabó and co-workers (25) found that supported Pd is an active catalyst for the synthesis of CH<sub>3</sub>OH from an H<sub>2</sub> + CO gas mixture at elevated pressure. It therefore appeared worthwhile to examine the catalytic performance of Pd catalysts in the hydrogenation of CO<sub>2</sub> in greater detail.

### EXPERIMENTAL

**Methods.** Catalytic investigations were carried out in a flow reactor made from an 8-mm-i.d. Pyrex glass tube or, when the total pressure was 9.5 bar, an 8-mm-o.d. stainless-steel tube. The dead volume was filled with glass beads. The reactor was heated by an external oven. No increase in

catalyst temperature was observed during the reaction. The ratio of H<sub>2</sub>/CO<sub>2</sub> or H<sub>2</sub>/CO in the reacting gas mixture was in general 4/1 or 3/1, respectively. Helium was used whenever a diluent was needed. High space velocities of 3000–6000 h<sup>-1</sup> were used. The conversion was in general less than 5–7%. The absence of diffusional limitation was confirmed by the method suggested by Körös and Nowak (27). Analyses of the exit gases were performed with a Hewlett-Packard 5750 gas chromatograph equipped with an HP 3370 electronic digital integrator. A 2-m-long, 0.25-in.-diam column packed with Porapak QS allowed complete separation of reactants and products. The amount of catalyst used was 0.3–0.6 g.

In the high-temperature IR cell, which was similar to that described earlier (26), the spectra were taken at the reaction temperature in the gas flow. The IR spectra were recorded with a Specord 75 IR Zeiss Jena double-beam spectrometer.

The dispersion of the supported metals was determined, as in our previous paper (1), by H<sub>2</sub>-O<sub>2</sub> titration at 298 K, using the pulsed flow technique.

**Materials.** The preparation of the catalysts has been described in the previous paper (1). They were produced by incipient wetness impregnation of supports with PdCl<sub>2</sub> solution, assumed to be H<sub>2</sub>PdCl<sub>4</sub>. The Pd content was 1 or 5 wt%.

For catalytic studies, small fragments of slightly compressed pellets were used. For IR spectroscopic measurements the powdered material was pressed into a 10 × 30-mm self-supporting plate. The sample thickness varied in the range 15–20 mg/cm<sup>2</sup>.

Before the catalytic measurements, the sample was oxidized in an O<sub>2</sub> flow for 30 min and reduced in a H<sub>2</sub> stream for 30 min at 673 K *in situ*, or the dried powder was heated in a flow of 40 ml H<sub>2</sub>/min, at a heating rate of 40°/min, up to 673 or 573 K and kept there for 60 min. After reduction the sample was cooled to the reaction temperature in flowing He.

The characteristic data on the supported Pd samples are shown in Table 1.

The gases used were initially of commercial purity. They were carefully purified by fractional distillation (CO<sub>2</sub>) or by adsorbing the impurities with a molecular sieve at the

TABLE 1  
Kinetic Data for the Hydrogenation of CO<sub>2</sub> and CO on Supported Pd Samples at 1 atm

Catalyst	Pd dispersion <sup>a</sup> (%)	N <sub>CH<sub>4</sub></sub> (× 10 <sup>13</sup> at 573 K)	N <sub>CO</sub>	Conversion of CO <sub>2</sub> (%)	E <sub>CH<sub>4</sub></sub> (kJ/mol)	A (s <sup>-1</sup> atm <sup>-x-y</sup> )	E <sub>CO</sub> (kJ/mol)	N <sub>CH<sub>4</sub></sub> <sup>b</sup> (× 10 <sup>3</sup> at 573 K)
5% Pd/Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	(40.2), 20.0	3.90	—	1.5–0.2	81.4	1 × 10 <sup>7</sup>	—	0.34
5% Pd/Al <sub>2</sub> O <sub>3</sub>	19.6	3.5	0.25	3.2–0.3	82.0	9 × 10 <sup>6</sup>	43.1	1.3
5% Pd/Al <sub>2</sub> O <sub>3</sub>	18.7	3.9	0.3	5.5–0.5	97.5	1 × 10 <sup>7</sup>	—	—
1% Pd/Al <sub>2</sub> O <sub>3</sub>	5.4	2.68	37.4	1.5–0.4	81.6	6.9 × 10 <sup>7</sup>	56.9	—
5% Pd/Al <sub>2</sub> O <sub>3</sub>	4.4	3.4	16.5	6.0–1.5	81.6	8.7 × 10 <sup>6</sup>	43.5	3.3
5% Pd/TiO <sub>2</sub>	6.5	16.3	16.0	7 –0.5	103.8	4.19 × 10 <sup>7</sup>	57.7	16.3
1% Pd/TiO <sub>2</sub>	5	79.5	(150)	15	—	—	—	—
5% Pd/SiO <sub>2</sub>	7.5	0.07	1.25	0.8–0.2	78.3	1.8 × 10 <sup>5</sup>	61.2	—
5% Pd/SiO <sub>2</sub>	14.7	0.20	3.14	6.5–1.2	108.8	5.17 × 10 <sup>5</sup>	54.4	0.1
5% Pd/MgO	9.6	0.03	4.27	6.5–2.1	156.1	6.95 × 10 <sup>4</sup>	67.4	0.05

<sup>a</sup> Average value determined by H<sub>2</sub>-O<sub>2</sub> titration at 298 K.

<sup>b</sup> H<sub>2</sub> + CO reaction. N<sub>CH<sub>4</sub></sub>, N<sub>CO</sub> = turnover frequencies (molecules formed/metal site × second) at the steady state. The reproducibility of turnover frequencies is better than 10%.

<sup>c</sup> In this case, the initial dispersity of the Pd (~40%) decreased to 25–20% during the reaction. In the calculation of turnover frequency the latter value (20%) was used.

temperature of liquid air. Helium was deoxygenated with an "Oxy-Trap" and "Indicating Oxy-Trap" (Altech Co.).

## RESULTS

### *Kinetic Measurements at Atmospheric Pressure*

The hydrogenation of  $\text{CO}_2$  on alumina-supported Pd catalysts occurred at a measurable rate above 520 K. Before kinetic measurements, the catalyst sample was treated with the reacting gas mixture at the highest reaction temperature (573–600 K, ~6%  $\text{CO}_2$  conversion). The products of the reaction were CO and  $\text{CH}_4$ . During the conditioning period, no significant changes were observed in the rate of  $\text{CO}_2$  conversion or in the product distribution.

On highly dispersed Pd (5% Pd/ $\text{Al}_2\text{O}_3$ ,  $D \approx 40\%$ ), the main product of the reaction was methane; CO was formed only in traces. In this case we observed a significant decrease in the dispersion of the Pd, to about 20–25%, during the reaction. However, no changes in the dispersion were experienced for other Pd samples. When the dispersion of the Pd was very low ( $D \approx 5\%$ ), the selectivity toward methane was only 15–20%. If the temperature was lowered, the selectivity of  $\text{CH}_4$  formation decreased.

A similar observation was made for other supported Pd samples. The reaction occurred at the lowest temperatures on Pd/ $\text{TiO}_2$ , and at the highest temperatures on Pd/ $\text{MgO}$ . Product distribution is shown in Fig. 1.

The dependence of the rate of methanation on the partial pressures of  $\text{CO}_2$  and  $\text{H}_2$  was determined for 5% Pd/ $\text{Al}_2\text{O}_3$  ( $D = 19\%$ ) from the slopes of log–log plots of the rate against the reactant partial pressure. It was found that the kinetic order for  $\text{CO}_2$  was nearly 0.5 (0.42) and that for  $\text{H}_2$ , 1 (1, 2).

The activation energy of the reaction was determined from the temperature dependence of the rate of  $\text{CH}_4$  and CO formation in the steady state. The activation energy of

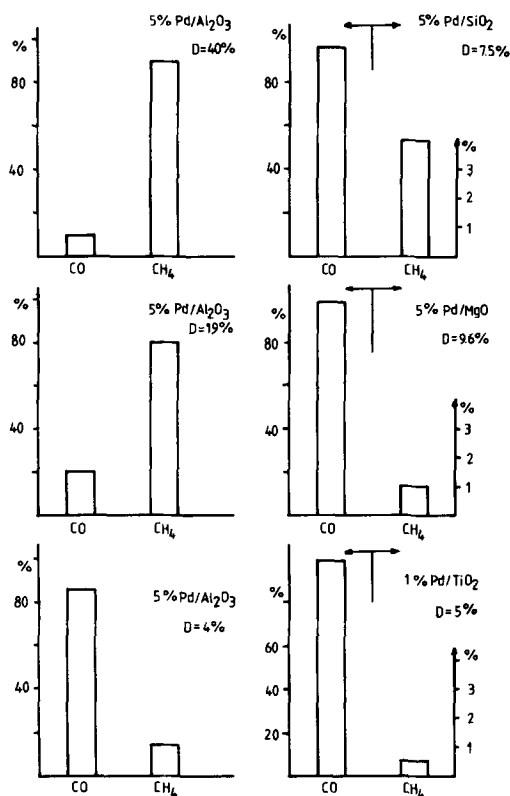


FIG. 1. Product distribution (in mol%) for the  $\text{H}_2 + \text{CO}_2$  reaction at 1 atm on different Pd samples at the steady state and at 523 K.

$\text{CH}_4$  formation fell in the range 78–108  $\text{kJ mol}^{-1}$  for Pd/ $\text{Al}_2\text{O}_3$ , Pd/ $\text{TiO}_2$ , and Pd/ $\text{SiO}_2$ . The activation energy of CO formation was lower (~57  $\text{kJ/mol}$ ); this was determined on samples containing Pd of low dispersion. The activation energies were higher for both reactions on Pd/ $\text{MgO}$ . Some Arrhenius diagrams are shown in Fig. 2.

The specific activities of the catalysts (in terms of turnover frequency) were calculated for all Pd samples. These values are given in Table 1. The turnover frequency for  $\text{CH}_4$  formation was the highest on Pd/ $\text{TiO}_2$ , its specific activity being more than one order of magnitude higher than those of Pd/ $\text{SiO}_2$  and Pd/ $\text{MgO}$ . The high efficiency of Pd/ $\text{TiO}_2$  was exhibited in CO formation (low Pd dispersion) too, where qualitatively the same activity order was found as for  $\text{CH}_4$  production.

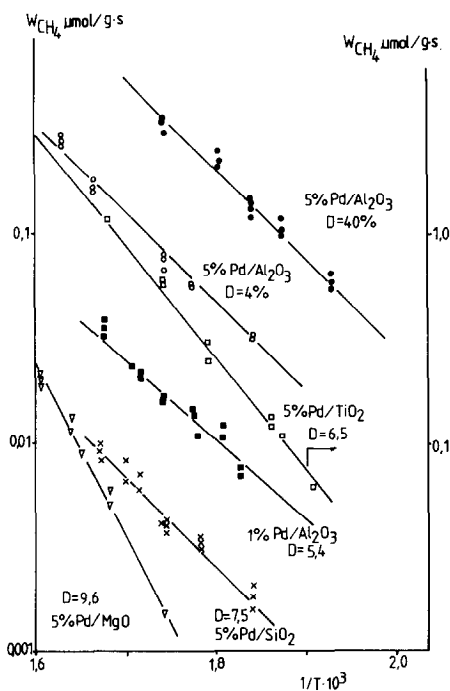


FIG. 2. Arrhenius plots of CH<sub>4</sub> formation in the H<sub>2</sub> + CO<sub>2</sub> reaction at 1 atm on various Pd samples.

### Infrared Spectroscopic Measurements during the Catalytic Reaction

To identify the surface species formed during the catalytic reaction, *in situ* IR spectroscopic measurements were performed in a flow and in a closed circulation system. Some spectra for a Pd/Al<sub>2</sub>O<sub>3</sub> sample are given in Fig. 3. Upon introduction of the H<sub>2</sub> + CO<sub>2</sub> (4:1) mixture at 523–573 K, absorption bands appeared at 1380, 1590, ~1850, ~1910, and 2060 cm<sup>-1</sup>. From a consideration of the IR spectra of adsorbed CO and formic acid on the same supported Pd catalysts (1), the bands at 1596 and 1380 cm<sup>-1</sup> are assigned to the asymmetric and symmetric O–C–O stretching vibrations of adsorbed formate ion. The bands at 1850, 1910, and 2060 cm<sup>-1</sup> are attributed to different types of adsorbed CO on Pd. An absorption band due to carbonate species appeared at 1450 cm<sup>-1</sup>. No, or only extremely weak, bands due to the CH stretching vibration were detected at 2915–2925 cm<sup>-1</sup>.

The intensities of formate bands varied

only slightly with the reaction time during the catalytic reaction. An increase was observed in the intensities of the CO bands, however, particularly in the case of Pd/Al<sub>2</sub>O<sub>3</sub> with a high Pd dispersion. These bands appeared in the spectrum even below the reaction temperature at 423–473 K. Their intensities were higher than at 523 K. When the temperature was raised to 573 K, new steady-state values were immediately attained. Upon further increase of the reaction temperature, the intensities of these bands were lowered. In Fig. 3B the intensities of various absorption bands obtained at different reaction temperatures are plotted as a function of time. In these cases the temperature of the sample was gradually raised from 423 K.

Injection of HCOOH vapor or CO into the gas mixture temporarily enhanced the intensities of the bands due to chemisorbed formate and CO, but after a relatively short time (3–5 min) they displayed the original steady-state values.

When the CO<sub>2</sub> in the gas mixture was replaced with He at 548 K, the intensities of the formate and CO bands decreased rapidly. This phenomenon also occurred when H<sub>2</sub> was replaced by He, but much more slowly.

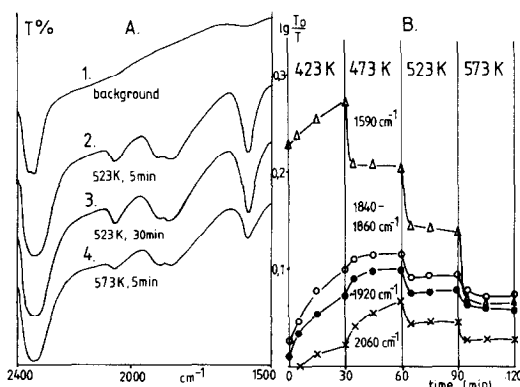


FIG. 3. (A) Infrared spectra taken during the H<sub>2</sub> + CO<sub>2</sub> reaction on 5% Pd/Al<sub>2</sub>O<sub>3</sub> ( $D = 19\%$ ) at 523 and 573 K. (B) Changes in intensities of various bands developed during the H<sub>2</sub> + CO<sub>2</sub> reaction at different temperatures on 5% Pd/Al<sub>2</sub>O<sub>3</sub> ( $D = 19\%$ ).

Qualitatively the same picture was obtained for Pd/MgO. The intensities of the bands due to adsorbed CO and formate species were much less than on Pd/Al<sub>2</sub>O<sub>3</sub> under the same conditions. In the case of Pd/SiO<sub>2</sub>, a very weak band was observed in the CO stretching region at 1910 cm<sup>-1</sup>, and there was no indication of the formation of formate ion. The low transmittance of the Pd/TiO<sub>2</sub> sample in the presence of an H<sub>2</sub> + CO<sub>2</sub> mixture prevented the performance of detailed IR spectroscopic measurements during the catalytic reaction.

#### Formation and Reactivity of Surface Carbon

In the case of supported Rh catalysts, we found a considerable amount of carbon deposited on the surface during the hydrogenation of either CO<sub>2</sub> or CO (11, 30). To determine the amount of unreacted carbonaceous species in the present case, the reaction was performed at 573 K for 60 min, and the surface of the catalyst was then flushed with a He stream for 10 min at the same temperature. The IR spectroscopic measurements indicated that this treatment is sufficient to remove all chemisorbed species from the surface. Afterward, H<sub>2</sub> was passed through the reactor. Significant methane production was observed for the next 10–20 min. The initial rate of methane formation after the H<sub>2</sub> + CO<sub>2</sub> reaction was practically the same as that observed during the catalytic reaction in the steady state, but it fell quickly. In contrast, after the H<sub>2</sub> + CO reaction, the rate of CH<sub>4</sub> formation during treatment of the surface with H<sub>2</sub> was about five times higher in the first few minutes than during the H<sub>2</sub> + CO reaction (Fig. 4). As no chemisorbed species remained on the catalyst surface after He treatment, it may be assumed that the observed CH<sub>4</sub> evolution is due to the hydrogenation of surface carbon. However, we cannot exclude the possibility that other carbon-containing species, which escaped detection by IR spectroscopy, also reacted with H<sub>2</sub> to yield CH<sub>4</sub>.

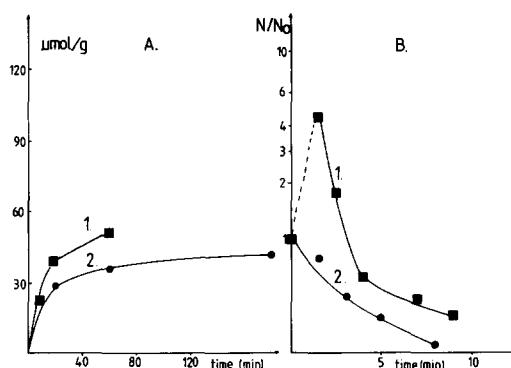


FIG. 4. (A) Amount of carbonaceous species formed in the H<sub>2</sub> + CO (1) and H<sub>2</sub> + CO<sub>2</sub> (2) reactions at 573 K on 5% Pd/Al<sub>2</sub>O<sub>3</sub> ( $D \approx 19\%$ ). (B) Relative rates of CH<sub>4</sub> formation on 5% Pd/Al<sub>2</sub>O<sub>3</sub>.  $N_0$  = turnover frequency of CH<sub>4</sub> formation at the steady state of the reaction.  $N$  = turnover frequency of CH<sub>4</sub> formation following steady-state reaction in the absence of CO (1) or CO<sub>2</sub> (2).

For Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, the formation of this carbonaceous species was followed as a function of the reaction time by means of the same method. The results obtained are shown in Fig. 4. The amount of carbonaceous species increased in time during both reactions; it was less in the H<sub>2</sub> + CO<sub>2</sub> reaction, where it soon approached a nearly steady value. The ratio of carbonaceous species to surface Pd, in terms of C<sub>s</sub>/Pd<sub>s</sub>, was about 0.5 (at 60 min) for the highly dispersed Pd ( $D \approx 20\%$ ).

#### H<sub>2</sub> + CO Reaction at Atmospheric Pressure

The catalytic performance of the Pd samples was examined in the H<sub>2</sub> + CO reaction under the same experimental conditions and in the same temperature range. The conversion of CO was low (1–3%). The primary aim of this study was only to acquire data comparable with those obtained in the hydrogenation of CO<sub>2</sub>. Whereas only two products, CH<sub>4</sub> and CO, were formed in the hydrogenation of CO<sub>2</sub>, in the hydrogenation of CO, ethane, propane, methanol, dimethyl ether, and acetaldehyde were also observed. The product distribution varied with the temperature and also with the na-

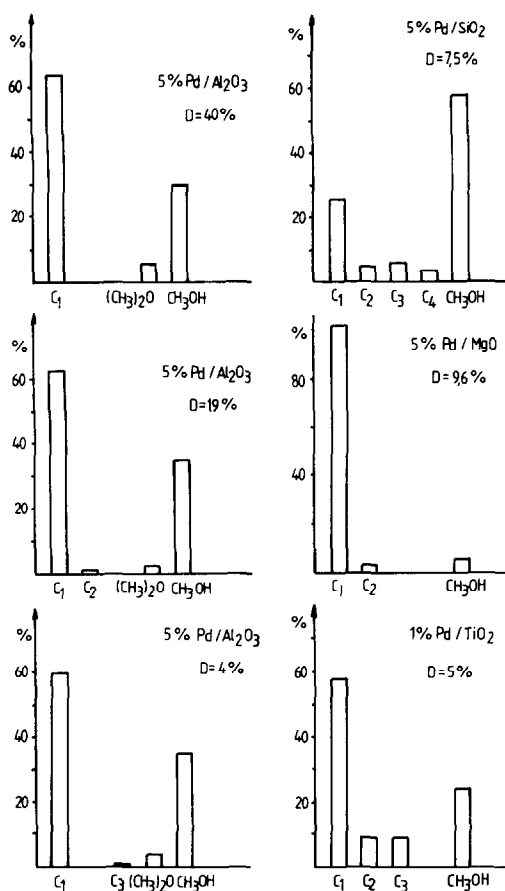


FIG. 5. Product distribution (in mol%) for the H<sub>2</sub> + CO reaction at 1 atm on different Pd samples at the steady state and at 548 K.

ture of the support (Fig. 5). It appears that the selectivity of hydrogenation of CO is only slightly affected in the dispersion range 4–40% for Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, at atmospheric pressure.

With respect to the effect of support on methanol formation, methanol was produced with higher selectivity on Pd/SiO<sub>2</sub> than on Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/TiO<sub>2</sub>. The amount of CH<sub>3</sub>OH increased slightly during the conditioning period; it exhibited a maximum with the variation of temperature (~533 K for Pd/Al<sub>2</sub>O<sub>3</sub>). The specific rates of CH<sub>4</sub> formation are shown in Table 1. The most active catalyst in CH<sub>4</sub> production is Pd/TiO<sub>2</sub>. The rate of CH<sub>4</sub> formation on this sample was two orders of magnitude higher than on the less active Pd/MgO.

### H<sub>2</sub> + CO<sub>2</sub> Reaction at 9.5 bar

In the H<sub>2</sub> + CO<sub>2</sub> reaction at 9.5 bar, formation of methanol was observed in addition to that of CO and CH<sub>4</sub>. Traces of ethane and propane (and dimethyl ether on alumina-supported Pd) were detected only occasionally.

During the conditioning period, the amounts of CO and CH<sub>4</sub> changed only slightly, but the amounts of methanol and other oxygenated species increased as time passed. For example, in the case of 5% Pd/Al<sub>2</sub>O<sub>3</sub> ( $D \approx 4\%$ ), the stable activity of the catalyst for methanol formation was achieved after 90 min of reaction at 523 K. The plot of the amount of methanol formed versus temperature exhibits a maximum in the interval 520–570 K on different Pd catalysts (Fig. 6). The product distributions determined on Pd catalysts are shown in Fig. 7. Not only does the ratio of CO to methane change with the dispersion of the catalyst, as experienced earlier at 1 atm, but the selectivity toward methanol is also dependent on it. On highly dispersed Pd (5% Pd/Al<sub>2</sub>O<sub>3</sub>,  $D \approx 40\text{--}25\%$ ), only traces of methanol were detected, but on Pd of low dispersion (~4%) the selectivity for methanol at 523 K was about 20% higher than that for methane.

Kinetic data on product formation as related to amount of catalyst and to surface Pd atoms are collected in Table 2. It can be

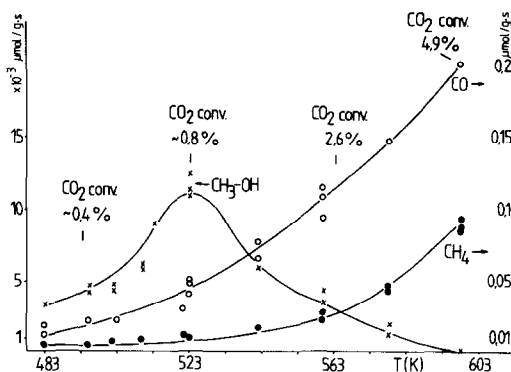


FIG. 6. Effect of temperatures on the formation of CH<sub>3</sub>OH, CH<sub>4</sub>, and CO on 5% Pd/Al<sub>2</sub>O<sub>3</sub> ( $D = \sim 4\%$ ) in the hydrogenation of CO<sub>2</sub> at 9.5 bar.

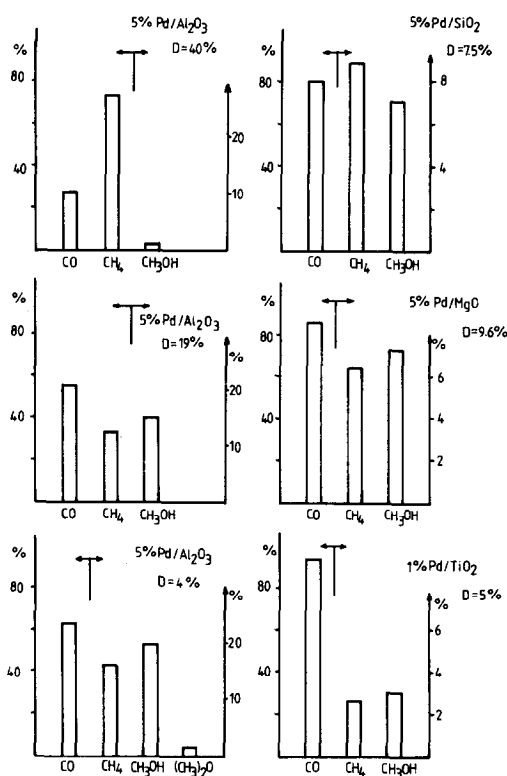


FIG. 7. Product distribution (in mol%) for the  $H_2 + CO_2$  reaction at 9.5 bar on different Pd samples at the steady state and at 523 K.

seen that the conversion of  $CO_2$  is the highest on  $Pd/TiO_2$  at this pressure too. Thus, it exhibited the highest specific activity in both methanol and methane production. For comparison, we investigated the hydrogenation of CO ( $H_2 + CO$ , 2:1) on the same catalysts and under the same conditions. The kinetic data obtained are also shown in Table 2.

## DISCUSSION

### General Features

The hydrogenation of  $CO_2$  on supported Pd catalysts was measurable under dynamic conditions above 520 K. The only hydrocarbon detected at atmospheric pressure was  $CH_4$ , which is in contrast to the hydrogenation of CO on the same Pd catalysts, where several other products, including  $CH_3OH$ , were formed.

As concerns the direction of the  $H_2 + CO_2$  reaction, it appears that only the dispersion of Pd plays a governing role, the nature of the support having only a minor effect. On a highly dispersed Pd sample, the reaction proceeds almost exclusively in the direction of  $CH_4$  formation, while on poorly

TABLE 2

Formation of  $CH_3OH$  on Supported Pd Catalysts in the  $H_2 + CO_2$  (4:1) and  $H_2 + CO$  (2:1) Reactions at 9.5 bar and 548 K

Catalyst	Pd dispersion (%)	$W_{CH_4}^a$	$W_{CH_3OH}$	$W_{ox}$	$N_{CH_4}$	$N_{CH_3OH}$	$S_{CH_3OH}$	Conversion of $CO_2$ or CO (%)
			( $\mu\text{mol/g} \cdot \text{s}$ )		( $\times 10^3$ )			
1% Pd/ $Al_2O_3$	4.4							
$H_2 + CO_2$		0.009	0.001	0.012	2.55	0.32	5.4	1.2
$H_2 + CO$		0.014	0.025	0.037	3.72	6.65	49.1	0.23
1% Pd/ $TiO_2$	5							
$H_2 + CO_2$		0.013	0.008	0.008	3.1	1.99	1.98	3.9
$H_2 + CO$		—	—	—	—	—	—	—
5% Pd/ $SiO_2$	7.5							
$H_2 + CO_2$		0.010	0.008	0.008	0.23	0.19	9.5	0.8
$H_2 + CO$		0.009	0.17	0.181	0.22	4.02	89.0	0.7
5% Pd/ $MgO$	9.6							
$H_2 + CO_2$		0.006	0.006	0.006	0.15	0.15	7.8	0.77
$H_2 + CO$		0.004	0.016	0.016	0.09	0.37	96.5	0.65

<sup>a</sup>  $W$  = rate of product formation.  $W_{ox}$  = rate of formation of oxygenated compounds ( $CH_3OH$ ,  $(CH_3)_2O$ ).  $S_{CH_3OH}$  = selectivity of  $CH_3OH$  formation =  $W_{CH_3OH}/W_{\text{all products}}$ .

dispersed Pd (in the same temperature range and at the same conversion of CO<sub>2</sub>) the reverse water-gas shift reaction occurs. The selectivity of CH<sub>4</sub> formation in that case hardly exceeds 10%. Methanol formation at atmospheric pressure was not detected for any sample. At 9.5 bar, however, significant methanol production was observed on larger particles.

In our exploratory study we found that, of the Pt metals, alumina-supported Pd is the least effective catalyst in the methanation of CO<sub>2</sub> (4). Its specific activity was about one order of magnitude lower than that for the methanation of CO, in complete contrast to the behavior of Ru and Rh (4, 7, 11). Explanation of this behavior of Pd catalyst was one of the driving forces behind this study.

This comparison, however, was based on the  $N_{\text{CH}_4}$  values of the H<sub>2</sub> + CO reaction determined by Vannice (28), the only ones which were available at that time. The kinetic data obtained in the present work on the same samples and under the same conditions clearly indicate that the methanation of CO<sub>2</sub> proceeds at a rate faster than that of CO, even on the Pd catalyst. The  $N_{\text{CH}_4}$  value taken from the first work of Vannice (28) can be considered exceptionally high.

#### *Possible Mechanism of Hydrogenation of CO<sub>2</sub>*

There are two basic routes for the hydrogenation of CO<sub>2</sub> (7, 11):

- (i) through the production and subsequent hydrogenation of CO, or
- (ii) through the formation of a surface intermediate different from that of the H<sub>2</sub> + CO reaction.

By means of IR spectroscopy we could identify absorption bands due to formate and chemisorbed CO. These surface species were formed even in the low-temperature (~300 K) interaction of H<sub>2</sub> + CO<sub>2</sub> on supported Pd (1). They were also detected in the hydrogenation of CO<sub>2</sub> on Rh and Ru catalysts (7, 11).

#### *Chemisorbed Formate*

Let us investigate first the possible roles of formate species. We presented previously (1) strong arguments that the formate species is located not on the Pd, but on the support which suggests that it cannot be a real surface intermediate in the methanation of CO<sub>2</sub> on supported Pd catalyst.

From the correlation between the absorbance of formate at 1580–1600 cm<sup>-1</sup> and its surface concentration (29), we obtain that the steady-state concentration of formate species during the reaction on Pd/Al<sub>2</sub>O<sub>3</sub> is 21.2 μmol/g at 548 K and 15 μmol/g at 573 K. Although these values are much lower than the number of surface Pd atoms, there is no reason to assume that the formate species detected during the hydrogenation of CO<sub>2</sub> are attached to the Pd.

However, it would be a mistake to consider it as a completely inactive surface species. The stability of the formate species on oxidic supports is lower in the presence of Pd, which indicates that during the reaction the formate species can migrate to the Pd, where it can decompose or react. Furthermore, it was demonstrated (Fig. 4) that the intensities of the formate bands are quite sensitive to the reaction conditions, and decrease somewhat more rapidly in the presence of H<sub>2</sub> than in He or CO<sub>2</sub>. We found the same behavior in the case of Rh/Al<sub>2</sub>O<sub>3</sub> (30, 31).

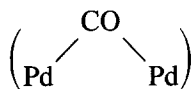
#### *Chemisorbed CO and Surface Carbon*

The fact that chemisorbed CO was detected even when the reaction produced almost exclusively CH<sub>4</sub> strongly supports the view that the hydrogenation of CO<sub>2</sub> occurs through the formation of CO. The results in Ref. (1) clearly show that the dissociation of CO<sub>2</sub> on Pd occurs to a well-detectable extent above 423 K, and the presence of H<sub>2</sub> greatly promotes this process. Evidence was also presented that a carbonaceous species, very probably surface carbon, is deposited during the catalytic reaction. Although Pd is considered not very reactive

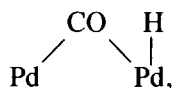


toward CO dissociation (25), we detected a limited disproportionation of CO on highly dispersed Pd. A value of 0.15 was obtained for the  $C_s/Pd_s$  ratio in 60 min at 573 K (36). This observation is in harmony with the recent report by Ichikawa *et al.* (32) that CO dissociates on small Pd particles, and that the low-temperature binding state of CO, as studied by TPD, is the one responsible for this reaction on Pd. The larger amount of carbonaceous species we found deposited on the Pd/Al<sub>2</sub>O<sub>3</sub> after the catalytic reaction (60 min at 573 K, at ~4% conversion) may indicate that the dissociation of CO is also promoted by hydrogen, or more precisely by adsorbed hydrogen.

The results of *in situ* IR spectroscopic measurements seem to be in harmony with these results and conclusions. The absorption band of the multiply bonded CO



appeared at lower frequency (1900–1920 cm<sup>-1</sup>) than in the presence of CO under the same conditions (1940–1960 cm<sup>-1</sup>). This was clearly demonstrated in the study of the H<sub>2</sub> + CO<sub>2</sub> surface interaction too, when the CO bands were more intense (1). In the interpretation of this shift we assume that in the presence of a large amount of gaseous dihydrogen, Pd–carbonyl hydride,



is formed and the shift is caused by the increase  $\pi$  donation from the Pd into the antibonding  $\pi$  orbital of the CO. The electron transfer from the H to the CO through the Pd increases the Pd–C bond strength and, at the same time, weakens the C–O bond on the surface.

We obtained strong IR evidence for the existence and the role of carbonyl hydride species in the hydrogenation of CO<sub>2</sub> and CO on supported Rh (11, 30, 33, 34),

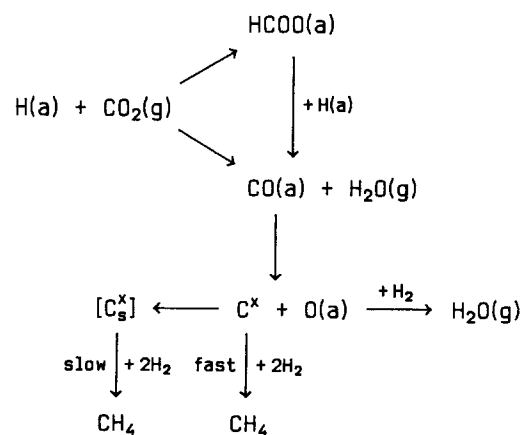
which was recently confirmed by Worley *et al.* (35) through the use of deuterium.

We note here that Vannice *et al.* (37) found a shift of the CO bands (0–40 cm<sup>-1</sup>) in the same direction in the presence of H<sub>2</sub>, while Palazov *et al.* (38) reported a shift to higher frequencies. This was interpreted by the formation of an electronegative  $\beta$ -hydrogen coadsorbed with CO on the Pd surface. While we cannot exclude the possibility that the sample preparation, particle sizes, and nature of support influence the formation and bonding of chemisorbed species, we also emphasize that different kinds of chemisorbed CO are formed in a surface reaction (i.e., bonded to different sites of the metal) and following CO adsorption at the same coverage. This was demonstrated in the low-temperature interaction of H<sub>2</sub> + CO<sub>2</sub> on Pd (1) and also in the case of Rh (33, 34, 39).

#### A Possible Mode of Hydrogenation of CO<sub>2</sub>

On the basis of the above considerations, we propose Scheme 1 for the methanation of CO<sub>2</sub> on supported Pd.

As the rate of methanation of CO<sub>2</sub> is higher than that of CO, the dissociation of CO<sub>2</sub> cannot be the rate-determining step. This conclusion is supported by our previous observation (1) that the dissociation of CO<sub>2</sub> occurs on supported Pd (particularly



SCHEME 1. C<sub>s</sub> = less reactive carbon.

in the presence of H<sub>2</sub>) at or above 423 K. Furthermore, the fact that surface carbon can accumulate on the catalyst surface does not automatically mean that its hydrogenation is the slow step.

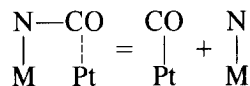
For Rh catalysts we demonstrated that the surface carbon formed in the dissociation of CO (CO<sub>2</sub>) during the methanation of carbon oxides at 548–573 K is easily hydrogenated to methane. Above 573 K, however, this carbon is rapidly transformed into a less reactive form (40). It seems very plausible that a significant portion of the surface carbon, found on Pd catalyst by 573 K, is already in a less reactive form, and its hydrogenation contributes only slightly to CH<sub>4</sub> production. Accordingly, it is most likely that the slowest step in the methanation of CO<sub>2</sub> is the *dissociation of adsorbed CO*.

It is very likely that the high activity of Pd/TiO<sub>2</sub> in the methanation reaction is due to its favorable effect on the dissociation of CO over Pd. We may assume that an electronic interaction occurs between reduced titania (the work function of reduced titania, Ti<sup>3+</sup>, is 4.6 eV (41)) and Pd (the work function of Pd is 5.12 eV (42)). As a result, the electron donation from Pd into an antibonding  $\pi$  orbital of the CO will be larger, which strengthens the Pd–C bond and weakens the C–O bond. As the electronic interaction between metal and Al<sub>2</sub>O<sub>3</sub> is smaller (43, 44), while it does not exist at all for MgO and SiO<sub>2</sub> support, the activity order of the catalyst samples seems to be in harmony with this picture. The exceptionally high catalytic activity of Rh/TiO<sub>2</sub> in the methanation of CO<sub>2</sub> and CO was also explained by this model (11, 30, 40, 45).

The possibility of an electronic interaction between metal catalyst and TiO<sub>2</sub> support was assumed by Szabó and Solymosi (43), who first attempted to demonstrate this in 1960 for the Ni/TiO<sub>2</sub> system. This idea has been applied by a number of authors to explain the high catalytic activity of TiO<sub>2</sub>-supported metals, but at the same time it has also been strongly criticized (50). As we discussed in a review (44) on

this topic, it cannot be expected that the *bulk* of the metal will be influenced by this electronic effect. A significant interaction, i.e., a more important electron-configuration change, is likely only *at the metal–support interface*, considered the “*active site*” for the catalytic reaction. In the present case, where the metal dispersion is relatively low, the number of these active sites is certainly very small. This is in the line with the conclusion of Vannice (37) that only a small fraction of the Pd surface is active for the hydrogenation of CO.

However, in addition to the above effect, the possibility cannot be excluded that the support can participate directly in the catalytic reaction, partly as a result of the activating effect of the metal; this view is currently receiving increasing attention. This idea was suggested by Bond as long ago as 1960 in the discussion of a paper dealing with the Ni/TiO<sub>2</sub> system (43), and was considered further in a review paper in 1967 (44). The decomposition of isocyanate surface species, NCO, on supported metal provided a good example of the activation of a surface species by both the metal and the support (51). IR spectroscopic evidence was presented that NCO adsorbs on the support via the N atom, but that it also interacts with the metal by forming a bond with the CO of the NCO, which promotes its decomposition.



The importance of the metal/support interface has recently been emphasized by Burch *et al.* (52). In a discussion of CO dissociation on M/TiO<sub>2</sub> catalysts, they suggested a direct interaction between Ti<sup>3+</sup> and the oxygen atom of a CO molecule, which promotes the dissociation of CO on M/TiO<sub>2</sub>.

It is possible that this effect may contribute to the high activity of Pd/TiO<sub>2</sub> in the present case too.

*As concerns methanol synthesis* it is in-

structive to compare the formation of methanol in the  $H_2 + CO_2$  reaction with that observed for the  $H_2 + CO$  reaction on the same samples and under the same conditions. It appears that the amount of methanol is more than one order of magnitude higher in the latter case. This feature is valid for practically all the catalyst samples. Thermodynamic calculations suggest that more methanol should be produced in the  $H_2 + CO_2$  than in the  $H_2 + CO$  reaction, which clearly indicates that kinetic factors play a dominant role.

If we assume that the hydrogenation of  $CO_2$  occurs through the formation of CO at higher pressure, too, the formation of methanol in the  $H_2 + CO_2$  system is preceded by the production of CO. In this case, the mechanism of methanol formation in the  $H_2 + CO_2$  mixture would be basically the same as that proposed for methanol synthesis from the  $H_2 + CO$  system (25, 46–48). As regards the different selectivity values for methanol formation, we may assume that in the  $H_2 + CO_2$  reaction, the hydrogen-assisted dissociation of CO occurs relatively to a greater extent, which favors methane production. In the case of the  $H_2 + CO$  reaction, due to the high surface concentration of adsorbed CO and to its poisoning effect, the hydrogen-assisted dissociation of CO is more limited, and therefore more methanol is produced.

This consideration is different from that proposed by Ramarosan *et al.* (49), who claimed that methanol synthesis from  $CO_2$  occurs by a direct reaction and not through production of CO and consecutive hydrogenation. They produced methanol from  $H_2 + CO_2$  at a much higher selectivity than from a  $H_2 + CO$  gas mixture. However, they worked at a higher pressure, 120 bar, and used  $La_2O_3$  as support. Further, the amount of CO formed was not taken into account in the calculation of the selectivity of methanol production! One might conclude that the reaction pathway of methanol synthesis from  $CO_2$  is influenced by the pressure range, the nature of the support,

and the surface concentration of adsorbed CO.

It has recently been assumed that formate is an important surface intermediate of methanol synthesis (48, 49), too. Although we found that the formate species can be hydrogenated to methane to a great extent (31), our attempts to produce methanol in the reaction between formate and hydrogen at atmospheric pressure have so far been unsuccessful. Experiments at high pressures are in progress.

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