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Catalytic reaction of methane with carbon dioxide over supported palladium

A. Erdöhelyi, J. Cserényi, E. Papp, F. Solymosi*

Institute of Solid State and Radiochemistry, A. József University and Reaction Kinetics Research Group of the Hungarian Academy of Sciences[†], P.O. Box 168, H-6701 Szeged, Hungary

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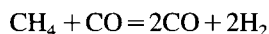
Abstract

The reforming of methane with carbon dioxide has been investigated at 673–773 K on supported palladium catalysts in a fixed-bed continuous-flow reactor. In addition, the dissociation of carbon dioxide and methane, and the reactivity of the surface carbon formed have also been examined. The dissociation of carbon dioxide, detected by infrared spectroscopy, occurred at the lowest temperature, 373 K, on Pd/TiO₂. It was greatly promoted by the presence of methane. The decomposition of methane at the temperature of the CH₄ + CO₂ reaction (ca. 773 K) proceeded initially at a high rate yielding hydrogen and small amounts of ethane and ethene. The deposition of surface carbon was also observed, which was hydrogenated only above 720 K. The reaction between carbon dioxide and methane occurred rapidly above 673 K to give carbon monoxide and hydrogen with a ratio of 1.3–1.7. Very little carbon was deposited during the reaction of a stoichiometric gas mixture. Kinetic parameters of the reaction were determined and a possible reaction mechanism is proposed.

Key words: carbon dioxide hydrogenation; kinetics; methane reforming; palladium

Introduction

Great efforts have recently been paid to the transformation of carbon dioxide and methane, the cheapest carbon-containing materials, into more valuable compounds in catalytic reactions [1–3]. One of the means of achieving this goal is to react carbon dioxide and methane with each other and produce synthesis gas [4–13]



*Corresponding author. Tel./fax. (+36-62) 322378, e-mail H3925REA@ELLA.HU

[†]These laboratories are part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

or even more valuable substances. This reaction has been commercialized as the Calcor process [4]. One of the most effective catalysts for this process is supported rhodium [5].

The high efficiency of rhodium was confirmed by our recent comparative study of alumina-supported platinum metals, when the rate of carbon dioxide reforming with methane was related to the number of surface metal atoms [11,12]. In the present paper, the $\text{CO}_2 + \text{CH}_4$ reaction is investigated on supported palladium which is a good catalyst for the reverse shift reaction [14,15]. Great attention is paid to the effects of the support and to the identification of surface intermediates in the low-temperature interaction and high-temperature reaction of carbon dioxide and methane.

Experimental

Materials

The catalysts were prepared by impregnating the support with a solution of PdCl_2 salts to yield a nominal 1 wt.-% or 5% metal. The following oxides were used: Al_2O_3 (Degussa P 110 Cl, $100 \text{ m}^2/\text{g}$), TiO_2 (Degussa P25, $150 \text{ m}^2/\text{g}$), SiO_2 (Cab-O-Sil, $200 \text{ m}^2/\text{g}$), and MgO (DAB 6, $170 \text{ m}^2/\text{g}$). For catalytic studies small fragments of slightly compressed pellets were used. The size of the fragments was $2 \times 2 \times 0.5 \text{ mm}$. For IR spectroscopic measurements the powdered material was pressed into a $10 \times 30 \text{ mm}$ self-supporting disk.

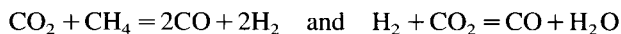
Before the measurements the catalysts were oxidized for 30 min and reduced for 60 min at 773 K in situ. After oxidation and reduction the sample was evacuated or flushed with helium or nitrogen for 15 min.

The gases used were initially of commercial purity. The carbon dioxide was further purified by fractional distillation. Helium (99.995%) and nitrogen (99.95%) were deoxygenated with an oxy-trap. The other impurities were adsorbed by a 5A molecular sieve at the temperature of liquid air.

Methods

The same experimental methods were used as described in our previous papers [11,12]. The decomposition of methane and the $\text{CH}_4 + \text{CO}_2$ reaction were carried out in a fixed-bed continuous flow reactor made from a 15-mm I.D. quartz tube. The amount of catalyst used was 0.5 g, the flow rate of reactant gases were 40 ml/min and the space velocities were 6000 h^{-1} . Helium or nitrogen was used as diluent to determine the partial order of carbon monoxide and hydrogen formation. The exit gases were analyzed gas chromatographically (Hewlett-Packard 5890 and 5710) on a Porapack QS column. The amounts of CO, CO_2 and CH_4 were determined in the helium carrier gas. Hydrogen was detected simultaneously in a separate gas chromatograph in a nitrogen stream by a thermal conductivity detector. The gas sampling valves of the gas chromatographs were connected with each other.

The conversion of carbon dioxide and methane were defined as the converted carbon dioxide or methane per total amount of carbon dioxide or methane. The methane and carbon dioxide consumption were calculated from the products, taking into account the following equation:



A pulse reactor was also employed (8-mm O.D. quartz tube), which was incorporated between the sample inlet and the column of the gas chromatograph (Hewlett-Packard 5710). One pulse contained 16.3 μmol gases. Usually a 0.3-g sample was used and the dead volume of the reactor was minimized with quartz beads. The reactor was heated by an external oven.

The temperature-programmed reaction (TPR) experiments (for the determination of surface carbon formed in methane decomposition) were carried out in the pulse reactor. After production of carbon, and flushing of the surface with helium at the temperature at which carbon was formed, the samples were cooled in a helium flow to 323 K. The flow was then switched to hydrogen, the sample was heated at 12 K min^{-1} , and the hydrocarbons formed were analyzed.

The infrared spectroscopic studies were made in a vacuum cell using self supporting wafers which underwent the same pretreatment as the catalyst. The spectra were recorded with a Specord M 80 IR Zeiss Jena double-beam spectrometer.

The dispersions of the supported metals were determined by $\text{H}_2\text{-O}_2$ titration at 298 K using the pulse technique [14,15].

Results

Dissociation of carbon dioxide

First, we examined the adsorption and dissociation of carbon dioxide on supported palladium. The most sensitive method for following these processes is IR spectroscopy, as carbon monoxide, the primary product of the dissociation is strongly bonded to the palladium. In accordance with our previous measurements [14,15], carbon dioxide does not adsorb on supported palladium at room temperature and no dissociation can be detected on the palladium surface free of adsorbed hydrogen. The same was observed for palladium single crystals [16–19]. However, the dissociation occurred at elevated temperatures, 473–673 K on supported palladium samples. The dissociation is indicated by the appearance of weak absorption bands in the region of 1750–2080 cm^{-1} due to adsorbed carbon monoxide with a different coordination. A weak carbon monoxide band at 1892 cm^{-1} , indicative of the dissociation of carbon dioxide, appeared at the lowest temperature, 373 K, in the IR spectrum of Pd/TiO₂ (Fig. 1). The intensity of the band remained practically unaltered up to 473 K, and disappeared above 573 K. On Pd/Al₂O₃ two carbon monoxide bands were observed at 1770 and 1870 cm^{-1} at 473 K. The intensities of these bands increased with increasing the adsorption temperature of carbon dioxide. On Pd/SiO₂ weak carbon monoxide bands, absorbing at 1810 and 1870 cm^{-1} (Fig. 1), were detected at and above 473 K. On increasing the temperature to 523 K, the latter peak shifted to 1910 cm^{-1} , and above 623 K new absorption bands at 1970 and 2079 cm^{-1} appeared. At the same time, the band at 1870 cm^{-1} also shifted to higher wavenumbers. Spectra obtained for different samples are shown in Fig. 1.

The dissociation of carbon dioxide was also studied by the pulse method at 773 K, at the

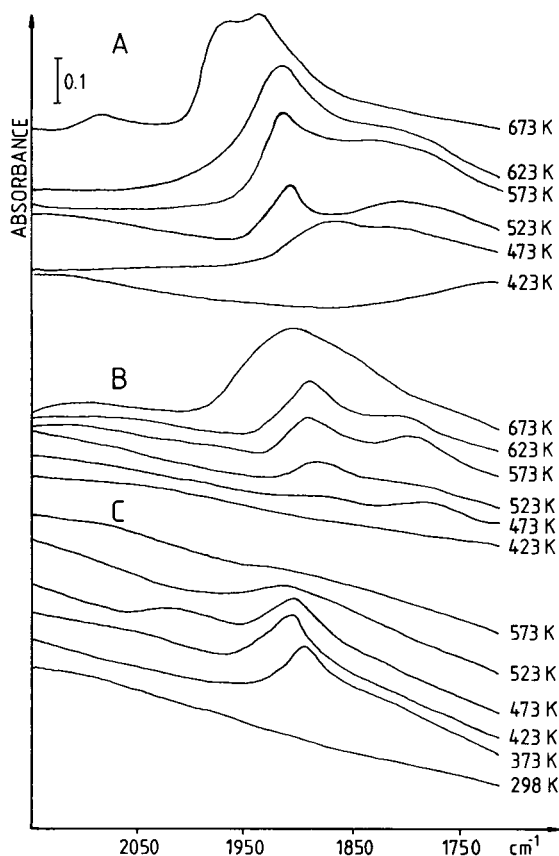


Fig. 1. Infrared spectra of supported Pd following the adsorption of carbon dioxide (50 Torr) at different temperatures. (A) 5% Pd/SiO₂, (B) 5% Pd/Al₂O₃, (C) 5% Pd/TiO₂. Spectra were always taken at 300 K.

catalytic reaction temperature of carbon dioxide with methane. The amount of carbon monoxide formed in the dissociation of carbon dioxide decreased in all cases as a function of pulse number. The highest amount of carbon monoxide was produced on Pd/TiO₂. On Pd/SiO₂ only traces of carbon monoxide were detected. The results are shown in Fig. 2. As the carbon monoxide formed can dissociate to carbon at such a high temperature, an attempt was made to determine the amount of surface carbon present: the catalyst was treated with oxygen pulses and the amount of carbon dioxide was determined. We found only a very small amount of carbon (0.01–0.5 μmol/g catalyst).

Decomposition of methane and the reactions of the formed carbon

The decomposition of methane was investigated under the experimental conditions of the CO₂ + CH₄ reaction. The formation of hydrogen, ethane and ethylene was established (Fig. 3). The amount of hydrogen greatly exceeded that of C₂ hydrocarbons on all catalyst

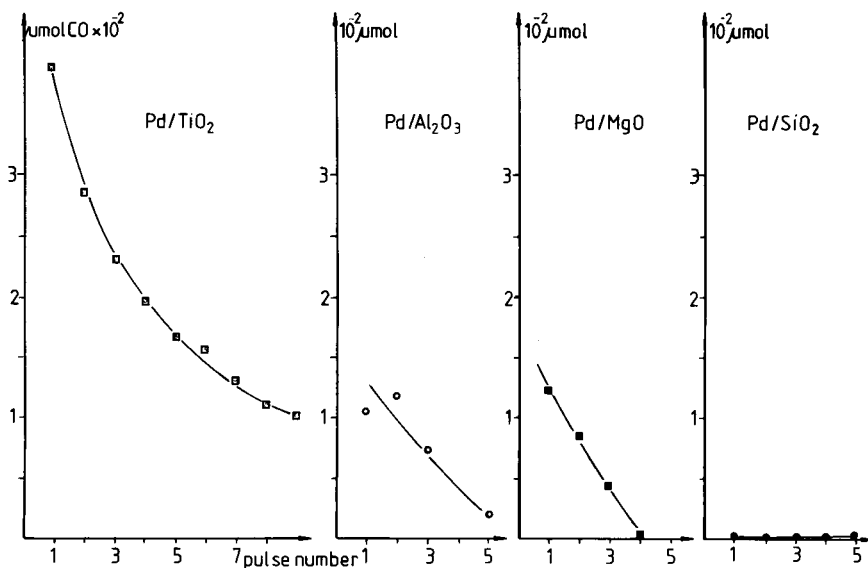


Fig. 2. The amount of CO formed in the dissociation of carbon dioxide pulses on different Pd samples (1% Pd) at 773 K. One pulse contained 16.3 μmol of CO₂.

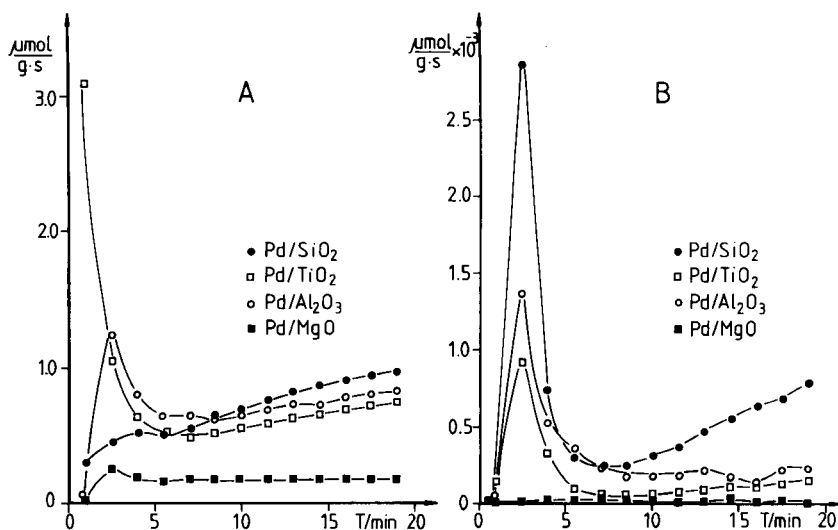


Fig. 3. Rates of H₂ (A) and C₂H₆ (B) formation in the decomposition of CH₄ on supported Pd (5% Pd) at 773 K. Flow-rate of N₂ + CH₄ (12.5%): 40 ml/min. Sample mass: 100 mg.

samples (Table 1). This suggests an accumulation of carbonaceous residue on the catalysts during methane decomposition. In the case of the most active Pd/TiO₂ catalyst the initial decomposition of methane, calculated from the hydrogen evolution, reached a value of

Table 1

Amount of ethane and hydrogen formed in the decomposition of methane on supported palladium catalysts at 773 K in 20 min^a

Catalysts	C ₂ H ₆ ($\mu\text{mol/g}$)	H ₂ ($\mu\text{mol/g}$)	C _s ^c ($\mu\text{mol/g}$)
5% Pd/TiO ₂	0.179	904	342
5% Pd/Al ₂ O ₃	0.3	786	386
5% Pd/SiO ₂	1.01 ^b	764	185
5% Pd/MgO	3×10^{-4}	183	89

^a12.5% methane in nitrogen was used as reactant; the flow rate was 40 ml/min.

^bSum of ethane and ethylene.

^cDetermined from the TPR curves of the hydrogenation of surface carbon up to 1100 K.

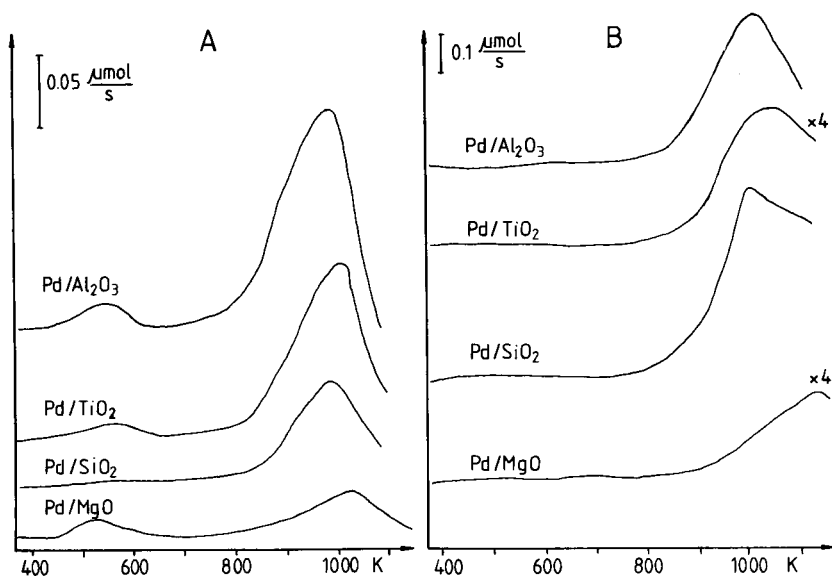


Fig. 4. Temperature-programmed reaction of carbon with H₂ on supported Pd (5% Pd). Carbon was produced by the decomposition of pure methane at 773 K for 1 min (A) and 15 min (B). Flow-rate of methane: 200 ml/min.

4.4%, but it decayed to 0.78% after 10 min. In this stage the activity of palladium samples was practically the same, with the exception of Pd/MgO, which exhibited much less catalytic effect on the decomposition of methane. The rate of ethane evolution passed through a maximum. The largest ethane formation was observed on Pd/SiO₂ (Fig. 3B). On this sample, the concentration of ethylene was commensurable with that of the ethane (C₂H₆/C₂H₄ ratio at the maximum of their formation was 2.08). On the other samples ethylene was only detected in the first minutes of methane decomposition.

The hydrogenation of surface carbon formed in the decomposition of methane at 773 K was investigated by the TPR method. Results are presented in Fig. 4. When the catalysts were pretreated with methane at 773 K for a short time (1 min, 200 ml), a small proportion

of surface carbon was hydrogenated between 450–600 K. The main reaction commenced on all samples only above 720 K, $T_{\max} = 980$ –1020 K. It appears that the support exerts only a slight influence on the reactivity of surface carbon. When the samples were exposed to methane for 15 min at 773 K, the low temperature TPR peaks were missing, but the high temperature features remained practically unaltered.

$CH_4 + CO_2$ surface interaction

In the subsequent experiments we examined how the addition of methane to carbon dioxide influenced the dissociation of the carbon dioxide. Some selected IR spectra for Pd/SiO₂ and Pd/Al₂O₃ are displayed in Fig. 5. It can be clearly seen that on Pd/SiO₂ a band at 1843 cm⁻¹ due to adsorbed carbon monoxide appears at lower temperatures (423 K), and with higher intensity as compared with the methane-free condition. The intensity of the

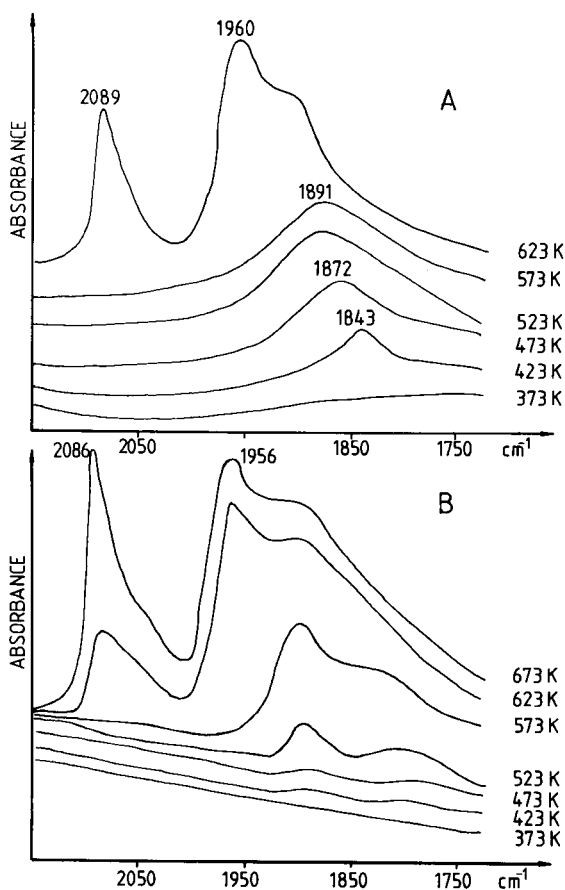


Fig. 5. Infrared spectra of supported Pd following the adsorption of CO₂ and CH₄ mixture at 50 Torr each at different temperatures. (A) 5% Pd/SiO₂ and (B) 5% Pd/Al₂O₃.

band increased, and its position shifted to higher wavenumbers when the temperature was raised further. At 623 K, an intense absorption band was detected at 2089 cm^{-1} . The effect of methane was more pronounced for Pd/Al₂O₃. Whereas in the absence of methane there was no indication of the high-frequency band of carbon monoxide above 2000 cm^{-1} , in the presence of methane it appeared with high intensity at and above 623 K.

Note that in spite of our great efforts, we did not succeed in identifying any of the absorption bands attributable to adsorbed CH₄ or CH_x species in the temperature range 300–623 K.

Reactions of methane with carbon dioxide

The highest reaction temperature applied was 773 K. Using a stoichiometric composition of reacting gas mixture, only a relatively slight deactivation of the catalyst samples occurred at this temperature (Fig. 6). In the case of Pd/SiO₂ and Pd/MgO the CO/H₂ ratio increased

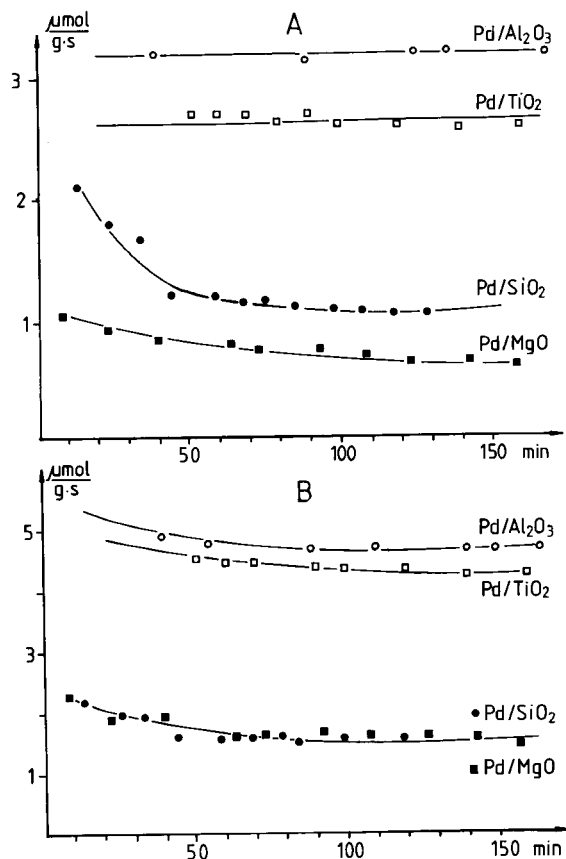


Fig. 6. Rates of H₂ (A) and CO (B) formation in the CO₂ + CH₄ reaction on different Pd samples (1% Pd) at 773 K.

at the beginning of the reaction. On the other samples it changed only slightly. In the temperature range 673–773 K, only traces of C_2 hydrocarbons were detected. A completely different picture was obtained when the reacting gas mixture contained excess methane. In this case a dramatic decay in the initial rate was experienced.

The effect of the reactant concentration on the rate of product formation was investigated on Pd/SiO₂. Reproducible results were obtained only at a stoichiometric composition and in an excess of carbon dioxide. With an increase in the concentration of methane and carbon dioxide the formation of both carbon monoxide and hydrogen increased (Fig. 7). At the same time the CO/H₂ ratio decreased. The kinetic orders were calculated from the logarithmic plots of the various rates versus the volume percentage of the reactant of interest. The orders with respect to methane were 0.15 and 0.32 for the formation of carbon monoxide and hydrogen, respectively. The order with respect to carbon dioxide was 0.12 for carbon monoxide formation and 0.24 for hydrogen evolution.

From the temperature dependence of the rates of hydrogen and carbon monoxide production, the apparent activation energies were determined (Fig. 8). On Pd/TiO₂ and Pd/Al₂O₃, we obtained higher values for the production of hydrogen than for that of carbon monoxide; as a result, a slight decrease in the CO/H₂ ratio was experienced with an increase of temperature. In the case of Pd/MgO, the activation energy of carbon monoxide formation was higher than that of hydrogen, and so the CO/H₂ ratio increased with increasing temperature. On Pd/SiO₂, the two activation energies were practically the same. Kinetic data are summarized in Table 2.

In order to compare the efficiencies of the supports, we calculated the turnover frequency, the rates of hydrogen and carbon monoxide formation related to the number of surface palladium atoms. The highest specific activity was obtained for Pd/TiO₂, which was fol-

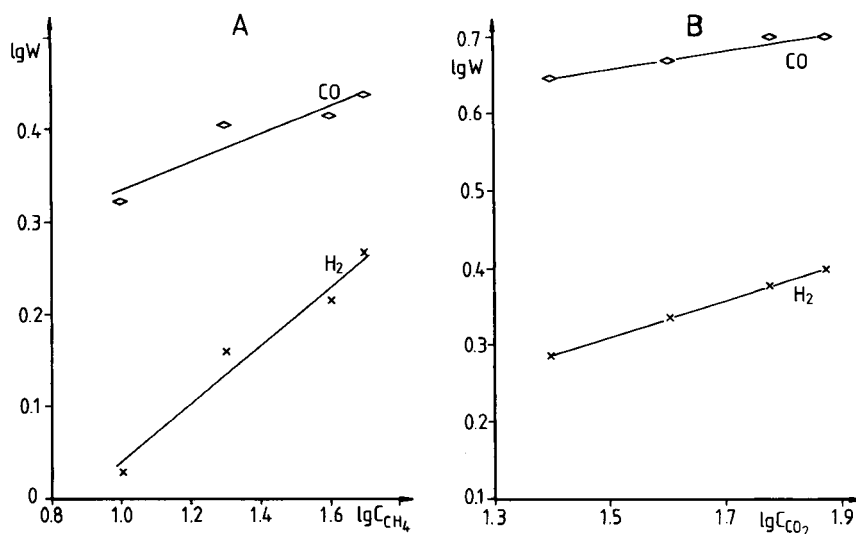


Fig. 7. Dependence of the rates (w [$\mu\text{mol/g}\cdot\text{s}$]) of product formation in $\text{CH}_4 + \text{CO}_2$ reaction on the partial pressure of CH_4 and CO_2 at 773 K. (A) Effect of CH_4 partial pressure. The CO_2 content was 25%. (B) Effect of CO_2 partial pressure. The CH_4 content was 25%. Inert gas (He or N_2) was used as diluent in both cases.

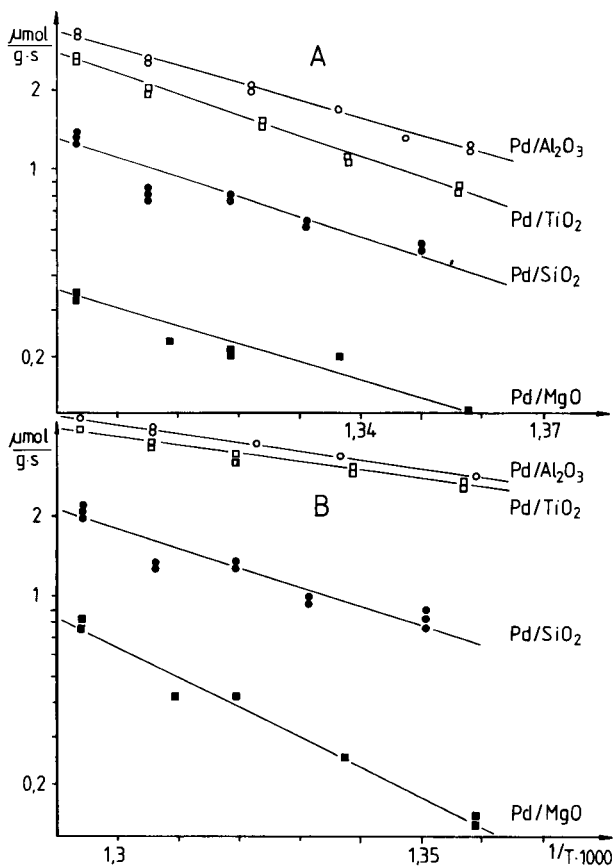


Fig. 8. Arrhenius diagrams of H_2 (A) and CO (B) formation for different Pd samples.

lowed by Pd/Al₂O₃, Pd/SiO₂, and Pd/MgO. The activity of Pd/TiO₂ was more than one order of magnitude higher than that of Pd/MgO (Table 2). As the dispersity of palladium on TiO₂ reduced at 773 K, significantly decreased due to the migration of titania on the palladium (“decoration effect”), the catalytic performance of the Pd/TiO₂ reduced at lower temperatures was also tested. In this case, the dispersity of palladium was commensurable with those measured for other palladium samples. Although the specific activity of the Pd/TiO₂ was somewhat lower than that of the high temperature reduced Pd/TiO₂, the Pd/TiO₂ still remained the most effective catalyst in the CH₄–CO₂ reaction. Note that the supports alone were completely inactive for this reaction up to 823 K.

Examination of catalyst samples after the CO₂ + CH₄ reaction revealed only a relatively small amount of carbon. The carbon was determined in the form of carbon dioxide by treating the catalysts with oxygen at 723–823 K. The highest value was obtained for Pd/SiO₂, but even in this case the ratio of C/Pd_{surf} was only 0.06. On other palladium samples only traces of carbon dioxide were detected.

Table 2
Some characteristic data for the CO₂ + CH₄ reaction on different supported palladium catalysts at 773K^a

Catalyst	<i>D</i> ^b (%)	Conversion (%)		Formation rate				CO/H ₂	<i>E</i> _{CH₄} (kJ mol)	<i>E</i> _{CO} (kJ mol)	<i>E</i> _{H₂} (kJ mol)	Surface carbon ^d C/Pd
				μmol/g · s		TOF ^c (s ⁻¹)						
				CH ₄	CO ₂	CO	H ₂					
1% Pd/TiO ₂	3.03	9.4	16.1	4.37	2.59	1.53	0.9	1.68	91.5	62.8	145.8	> 0.001
1% Pd/Al ₂ O ₃	23.2	8.6	15.0	4.72	3.16	0.21	0.14	1.47	93.1	62.8	125.7	> 0.001
1% Pd/SiO ₂	11.6	4.8	7.4	1.9	1.3	0.18	0.12	1.46	141.2	141.3	141.1	0.02
1% Pd/MgO	10.8	1.4	2.5	0.76	0.35	0.07	0.03	1.50	113.5	216.9	129.4	> 0.001

^aThe carbon dioxide and methane content of inlet gas was 50–50%.

^bDispersion: the amount of surface metal atoms.

^cTurnover frequency; rates related to the number of surface metal atoms.

^dThe amount of surface carbon formed in the first hour of the reaction. The carbon was determined in the form of carbon dioxide by treating the surface with oxygen at 773 and 873 K.

Discussion

Let us first consider the dissociation of carbon dioxide and methane on supported palladium at the catalytic reaction temperatures.

Dissociation of carbon dioxide

The dissociation of carbon dioxide on the samples used in the present study was monitored by IR spectroscopy and by the pulse method. Carbon monoxide bands at 1810–1820, 1870–1910, 1970 and 2079 cm⁻¹, indicative of the dissociation of carbon dioxide, appeared only at and above 373–473 K. The band at 1870–1910 cm⁻¹ relates to twofold coordinated carbon monoxide, and the band at 1810–1820 cm⁻¹ to threefold coordinated carbon monoxide [20,21]. The band at 2079 cm⁻¹ is ascribed to the linearly bonded carbon monoxide. The band at 1970 cm⁻¹ produced also above 623 K, has been attributed to the carbon monoxide adsorbed on (100) planes of palladium [22,23]. The fact that the latter two bands appeared only above 623 K (Pd/SiO₂) may be the result of carbon monoxide-induced agglomeration or morphological changes of palladium crystallites, as was observed at high temperatures for supported rhodium samples [24–26]. Alternatively, the surface concentration of carbon monoxide at lower temperatures was low enough to produce linearly bonded carbon monoxide species.

If the temperature at which the carbon monoxide bands appear is taken as a measure of the dissociation of carbon dioxide, then the order of activity of the palladium samples is as follows: Pd/TiO₂, Pd/Al₂O₃, Pd/SiO₂ and Pd/MgO. The same order of activity was found in the high-temperature dissociation (at 773 K) of carbon dioxide (Fig. 2), and also in the CH₄–CO₂ reaction. Possible reasons of this order of activity are presented in the discussion of the catalytic results.

Decomposition of methane

The dissociation of methane over a supported palladium catalyst have been observed even in the low-temperature range, 473–573 K, when hydrogen and a small amount of ethane were produced with the deposition of surface carbon [27]. In the temperature range of the $\text{CH}_4 + \text{CO}_2$ reaction (673–773 K), the extent of methane decomposition was greater and a much larger amount of surface carbon was produced. This led to a significant decay in the decomposition of methane, which, however, did not cease. This may mean that the carbon species formed a cluster on the palladium crystallite or migrated onto the support.

The data presented in Fig. 3 indicate that, apart from the initial stage, where Pd/TiO₂ exhibited high activity, there is no significant support effect in the decomposition of methane on the palladium catalyst. The same is valid for the reactivity of surface carbon produced in the decomposition of methane (Fig. 4). The carbon formed exhibited a rather low reactivity towards hydrogen, as its hydrogenation started only above 720 K. A more reactive carbon ($T_p = 520\text{--}550\text{ K}$) was detected only when the reaction time of the decomposition of methane (e.g. that of the carbon formation) was very short (Fig. 4). Taking into account our results obtained on the reactivity of different carbon forms over supported rhodium [12,28,29], these features suggest that in the high-temperature decomposition of methane a more reactive amorphous carbon is primarily produced which is quickly transformed into a less reactive graphitic form.

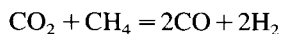
CH₄ + CO₂ interaction

From a comparison of the spectra presented in Figs. 1 and 5, it appears clearly that in the presence of methane the carbon monoxide bands develop at lower temperatures and at higher intensities than in the absence of methane. Accordingly, methane promotes the dissociation of carbon dioxide on supported palladium catalysts. As there was no spectral indication for the formation of any surface complexes between carbon dioxide and methane, the promotion of the dissociation of carbon dioxide is attributed to the effect of hydrogen formed in the decomposition of methane. It was demonstrated before that a small amount of hydrogen can greatly facilitate this process [14,15]. It is important to point out that this carbon monoxide band always appeared at lower frequencies than in the absence of methane. A down-shift of the carbon monoxide bands was also observed following the co-adsorption of the $\text{H}_2 + \text{CO}_2$ mixture on both supported rhodium and palladium catalysts and was ascribed to the formation of a carbonyl-hydride, $\text{Pd}_x \text{C}_x^{\text{H}}$ species [14,15,30,31]. It is assumed that the dissociation of carbon monoxide is promoted in this surface complex [30,31].

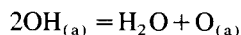
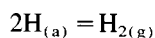
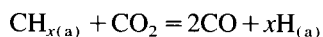
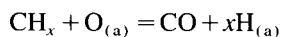
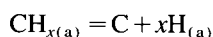
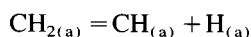
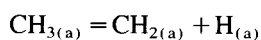
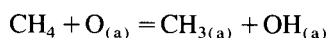
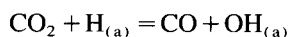
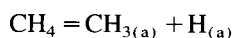
Catalytic reaction between CH₄ and CO₂

Although great attention is being paid to the conversion of carbon dioxide and methane to more valuable compounds, few papers have dealt with the catalytic reaction between carbon dioxide and methane [4–13], which is commercialized as the Calcor process [4].

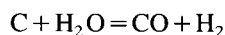
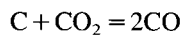
On the palladium samples used in the present study, the $\text{CH}_4 + \text{CO}_2$ reaction



proceeded with a significant conversion (0.5%–16%) at 673–773 K. Although both compounds undergo dissociation separately even at much lower temperatures, their decomposition products C, O and CO terminate their reactions by covering the active areas of the palladium metal. However, when both compounds are present, particularly at high temperatures, their self-decomposition is greatly accelerated. We assume the following effects: (i) promotion of the dissociation of carbon dioxide by hydrogen, and perhaps by CH_x fragments, too, and (ii) facilitation of the dissociation of methane by adsorbed O formed in the decomposition of carbon dioxide, which may activate the methane molecule. Accordingly, we may count with the following reactions:



Whereas the decomposition of methane on supported palladium in the absence of carbon dioxide produces a multilayer of carbon at the reaction temperature (Table 1), in the high-temperature reaction of $\text{CO}_2 + \text{CH}_4$ only a limited amount of surface carbon was produced. This suggests that the reactions of $\text{CH}_{x(a)}$ fragments with CO_2 and $\text{O}_{(a)}$ are very efficient; in other words, the possibility of decomposition of CH_x to the surface carbon is limited. Alternatively, the carbon (“status nascendi”) formed in the methane dissociation reacts with carbon dioxide and/or water immediately after its production,



before its aging and transformation into a less reactive form. Although we can not decide between the two alternatives at this stage of our work, we believe that the second alternative is less likely.

The fact that the ratio CO/H_2 was always higher than 1, and that it varied with the temperature and the catalyst, indicate the occurrence of several secondary processes, e.g. the hydrogenation of carbon monoxide and carbon dioxide, in this complex system. We note that the calculated equilibrium CO/H_2 ratio at 800 K is 1.65, and the conversions of methane and CO_2 are 20.6% and 30.8%, respectively [6].

The variation of the CO/H_2 ratio with the catalyst sample and with the temperature is probably due to the differences in the activation energy of the secondary reactions. For example the activation energy for methane formation in the $\text{H}_2 + \text{CO}_2$ reaction is much higher on Pd/MgO (156.1 kJ/mol) than on the other samples (81–103 kJ/mol) [14,15]. In contrast, the activation energies for methane formation in the $\text{H}_2 + \text{CO}$ reaction on the same catalyst were lower and differed only slightly from each other [14,15].

The rate of the $\text{CO}_2 + \text{CH}_4$ reaction on the palladium catalyst was very sensitive to the nature of the support. This is in contrast to the case of supported rhodium where no significant effect was established [12]. The specific activity of Pd/TiO₂ exceeded by almost one order of magnitude that of the less active Pd/MgO and Pd/SiO₂ (Table 2). The Pd/TiO₂ exhibited a higher activity even when it was reduced at 723 K, below the temperature of the development of the so-called "SMSI" effect. Similar results were obtained in the hydrogenation of carbon monoxide and carbon dioxide on supported palladium [14,15]. The order of activity of the palladium samples may be related to their efficiency in the dissociation of carbon dioxide, where the same order of activity was found. Accordingly in the case of supported palladium, the activation of carbon dioxide should play an important role in the $\text{CH}_4 + \text{CO}_2$ reaction. The high activity of Pd/TiO₂ may be associated with the extended electronic interaction between Pd and n-type TiO₂ [32] which increases the back donation of electrons from the palladium into π bonding of carbon dioxide thereby facilitating its dissociation and the formation of reactive oxygen required for the activation and reaction of methane. Alternatively, the oxygen vacancy present on titania promotes the dissociation of carbon dioxide.

Conclusions

(i) Methane decomposes on supported palladium samples at 773 to give hydrogen, a small amount of ethane and a carbonaceous residue. On Pd/SiO₂, the formation of ethylene was also observed. (ii) The carbon formed in the high temperature decomposition of methane is rather unreactive and hydrogenated only above 720 K. (iii) The dissociation of carbon dioxide occurred at elevated temperatures on all the palladium samples to give adsorbed carbon monoxide of different coordinations. In this case a significant support effect was established. The addition of CH₄ to CO₂ promoted the dissociation process. (iv) Supported palladium is an active catalyst in the high temperature reaction of $\text{CO}_2 + \text{CH}_4$ giving hydrogen and carbon monoxide with no or only very little carbon deposition. The order of activity of the catalysts, based on the turnover frequencies, is Pd/TiO₂ > Pd/Al₂O₃ > Pd/SiO₂ > Pd/MgO.

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