

## Activation of CH<sub>4</sub> and Its Reaction with CO<sub>2</sub> over Supported Rh Catalysts

A. ERDŐHELYI, J. CSERÉNYI, AND F. SOLYOSI

*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*<sup>1</sup>

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The dissociation of CH<sub>4</sub> and CO<sub>2</sub>, as well as the reaction between CH<sub>4</sub> and CO<sub>2</sub>, has been investigated over supported Rh in a fixed-bed continuous-flow reactor. The decomposition of methane on rhodium occurred above 423 K, when transient evolution of hydrogen and ethane were observed. The deposition of different kinds of carbon species was established, which led to the termination of the decomposition. The reactivity of surface carbon towards hydrogen exhibited a great variance, and sensitively depended on the conditions of its formation. The dissociation of CO<sub>2</sub> was detected by infrared spectroscopy only above 523 K, and it was promoted by the presence of CH<sub>4</sub>. The reaction between CO<sub>2</sub> and CH<sub>4</sub> proceeded rapidly above 673 K to give CO and H<sub>2</sub> with different ratios. No decay in the activity of Rh catalysts was experienced, and only very little, if any, carbon deposition was observed. The effects of different supports on all of the above processes have been examined. © 1993 Academic Press, Inc.

### 1. INTRODUCTION

We recently performed two comparative studies concerning the efficiency of supported Pt metals in the decomposition of CH<sub>4</sub> (1) and in the CH<sub>4</sub> + CO<sub>2</sub> reaction (2). In the first case we observed C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> production even at 473–573 K, the amounts of the products varying with the nature of the metal. A significant quantity of surface carbon was deposited, which reacted with hydrogen to produce CH<sub>4</sub> and higher hydrocarbons. Because of the accumulation of carbon, the ability of the catalyst to activate CH<sub>4</sub> decreased to almost zero in 10–15 min. As regards the decomposition of CH<sub>4</sub>, the most active metal was Ru/SiO<sub>2</sub>, whereas the highest amount of C<sub>2</sub>H<sub>6</sub> was produced on Pt/SiO<sub>2</sub>. The ability of Pt/SiO<sub>2</sub> to produce C<sub>2</sub>H<sub>6</sub> in the decomposition of CH<sub>4</sub> has been also observed by Belgued *et al.* (3).

Supported Pt metals exhibited high activ-

ity in the CH<sub>4</sub> + CO<sub>2</sub> reaction, to give CO, H<sub>2</sub>, and a small amount of C<sub>2</sub>H<sub>6</sub> at and above 773 K (2). The specific activities of the catalysts decreased in the sequence Ru, Pd, Rh, Pt, and Ir.

The present work reports more detailed kinetic measurements on supported Rh catalyst, with particular emphasis on the interaction of CH<sub>4</sub> with Rh and on the effects of the different supports. One of the reasons why Rh was selected for more detailed study is the industrial application of Rh/Al<sub>2</sub>O<sub>3</sub> in the CO<sub>2</sub> reforming of methane (Calcor process) (4).

In our early studies we found that, among the Pt metals, supported Rh is one of the most active catalysts in the hydrogenation of CO (5) and CO<sub>2</sub> (6, 7) and also in the dissociation of CO (8). The catalytic activity of Rh is strongly influenced by the nature of the support in all of the above reactions. An observation from these studies that is relevant to the present work is that the surface carbon formed in the dissociation of CO exhibited strikingly different reactivities towards hydrogen: the most reactive form, the carbidic species, reacted with H<sub>2</sub> to give

<sup>1</sup> This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

hydrocarbons at even slightly above room temperature (8).

## 2. EXPERIMENTAL

**Materials.** The catalysts were prepared by impregnating the support with the solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  salts to yield a nominal 1 wt% or 5% metal. The following oxides were used:  $\text{Al}_2\text{O}_3$ , (Degussa),  $\text{TiO}_2$  (Degussa P25),  $\text{SiO}_2$  (Cab-O-Sil), and  $\text{MgO}$  (DAB 6). The preparation of the catalysts has been described in the previous papers (5, 7).

For catalytic studies small fragments of slightly compressed pellets were used. For IR spectroscopic measurements the powdered material was pressed into a  $10 \times 30$ -mm self-supporting disk.

Before the measurements the catalysts were oxidized for 30 min and reduced for 60 min at 773 or 673 K *in situ*. After oxidation and reduction the sample was evacuated or flushed with He or  $\text{N}_2$  for 15 min.

The gases used were initially commercial purity. The  $\text{CO}_2$  was further purified by fractional distillation. He (99.995 %) and  $\text{N}_2$  (99.95%) were deoxygenated with an oxy-trap. The other impurities were adsorbed on a 5A molecular sieve at the temperature of liquid air.

**Methods.** 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 catalysts used was 0.5 g, and the space velocities were  $6000 \text{ h}^{-1}$ . The exit gases were analyzed gas chromatographically (Hewlett-Packard 5890 and 5710) on Porapak QS column. The  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  were determined in the He carrier gas, and  $\text{H}_2$  was detected simultaneously in the  $\text{N}_2$  stream by a thermal conductivity detector. The conversion of  $\text{CO}_2$  and  $\text{CH}_4$  were defined as the converted  $\text{CO}_2$  or  $\text{CH}_4$  per the total amount of  $\text{CO}_2$  or  $\text{CH}_4$ .

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. Usually a 0.3-g sample was used, and the dead

volume of the reactor was filled with quartz beads.

The temperature-programmed reaction (TPR) experiments were carried out in the pulse reactor. After production of carbon, and flushing of the surface with He at the temperature of the carbon formation, the samples were cooled in He flow to 323 K. The flow was then switched to  $\text{H}_2$ , the sample was heated at  $12 \text{ K min}^{-1}$ , and the hydrocarbons formed were analyzed (8).

The decomposition of  $\text{CH}_4$  was also investigated in the pulse reactor. In these cases after reduction of the samples (0.1 g), the reactor was flushed with  $\text{N}_2$ , the temperature of the catalyst was lowered to the reaction temperature and then the  $\text{N}_2$  stream was switched to  $\text{N}_2$  containing 12.5%  $\text{CH}_4$ . The amount of  $\text{H}_2$  formed was determined continuously with a thermal conductivity detector. The other products were determined in a separate experiment.

The infrared spectroscopic studies were made in a vacuum cell using a self supporting wafers which underwent the same pretreatment as the catalyst. The spectra were recorded with a Specord 75 IR Zeiss Jena double-beam spectrometer or with a FTIR (Bio-Rad FTIR 7) spectrometer.

The dispersions of the supported metals were determined by  $\text{H}_2$ - $\text{O}_2$  titration at 298 K using the pulse technique (5, 7).

## 3. RESULTS

### 3.1. Interaction of $\text{CH}_4$ with Rh

The interaction of  $\text{CH}_4$  with supported Rh was studied first in a flow system by analyzing the products formed. The evolution of  $\text{C}_2\text{H}_6$  and  $\text{H}_2$  was registered on every Rh sample. The amount of  $\text{H}_2$  was always higher than that of  $\text{C}_2\text{H}_6$ . The initial rate of  $\text{CH}_4$  decomposition was very high, but it decayed quickly to a very low value. More detailed measurements were performed on Rh/ $\text{SiO}_2$ .

As indicated by the production of hydrogen and ethane, the decomposition of methane was observed at as low as 423 K. With increase of the temperature, the rate of

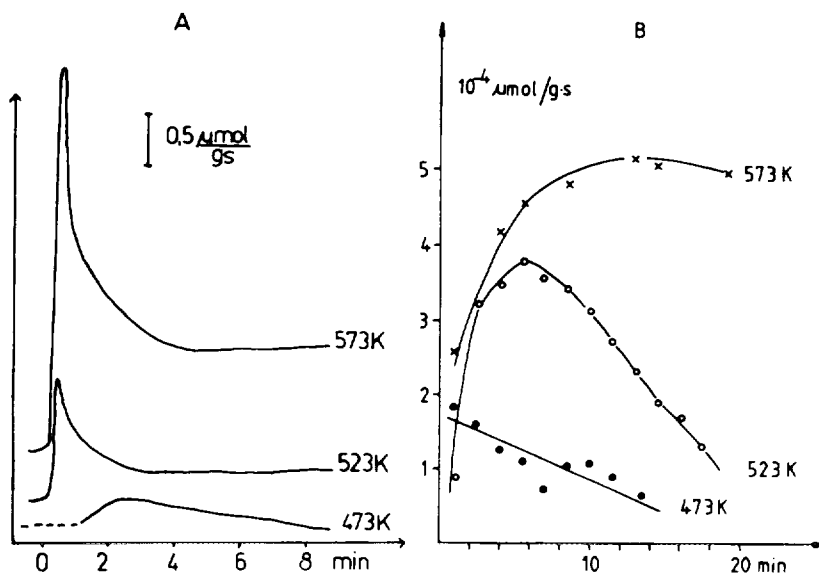


FIG. 1. Effects of temperature on the rates of H<sub>2</sub> (A) and C<sub>2</sub>H<sub>6</sub> (B) formation on 5% Rh/SiO<sub>2</sub>. Flow rate of N<sub>2</sub> + CH<sub>4</sub> (12.5%): 40 ml/min. The amount of catalyst: 0.1g.

product formation increased, but the C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> ratio did not vary significantly (Fig. 1).

The effects of supports on the reaction are displayed in Fig. 2. It appears that the rate of decomposition of CH<sub>4</sub> and the product distribution are influenced by the nature of the support. The most effective catalyst for the H<sub>2</sub> formation was the Rh/Al<sub>2</sub>O<sub>3</sub>, which was followed by Rh/TiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Rh/MgO, but the highest C<sub>2</sub>H<sub>6</sub> formation was observed on Rh/SiO<sub>2</sub>. The decomposition of CH<sub>4</sub> at the maximum of H<sub>2</sub> evolution was 44.3% for Rh/Al<sub>2</sub>O<sub>3</sub>, 25.4% for Rh/TiO<sub>2</sub>, 19.2% for Rh/SiO<sub>2</sub>, and 15.6% for Rh/MgO.

It is important to mention that no reaction of CH<sub>4</sub> occurred on the supports alone.

The large excess of hydrogen produced in the interaction of CH<sub>4</sub> with supported Rh indicated the partial or full decomposition of CH<sub>4</sub> to CH<sub>x</sub> or surface carbon. In order to identify the surface species formed, we first performed detailed infrared spectroscopic measurements. The experiments were carried out in the following sequence: the samples were degassed after reduction

at 673 K, the background spectra of reduced samples were taken at 200 K, the cell was then filled with CH<sub>4</sub> or with CH<sub>4</sub> + N<sub>2</sub> gas mixture, and the spectrum was registered again at 200 K. Afterwards the wafer was lifted into a CH<sub>4</sub>-containing flow in the zone preheated to 423–673 K, kept there for some minutes and then lowered back in to the cooled zone (200 K), where the IR spectrum was registered again in the presence of flowing CH<sub>4</sub>. The gas-phase spectrum of CH<sub>4</sub> was determined in a separate experiment and kept in the computer. In spite of great efforts, we did not succeed in identifying of any of the absorption bands attributable to CH<sub>x</sub> species, even when we analyzed the magnified difference spectra taken with a sensitive FTIR spectrometer. We paid particularly great attention to the frequency region 2800–3000 cm<sup>-1</sup>, where absorption bands due to adsorbed CH<sub>3</sub> species have been readily detected following the dissociation of CH<sub>3</sub>I on single-crystal surfaces (9–11) and on Pd/SiO<sub>2</sub> (12). Our failure to detect the transitory species of CH<sub>4</sub> dissociation is disappointing if we consider that the

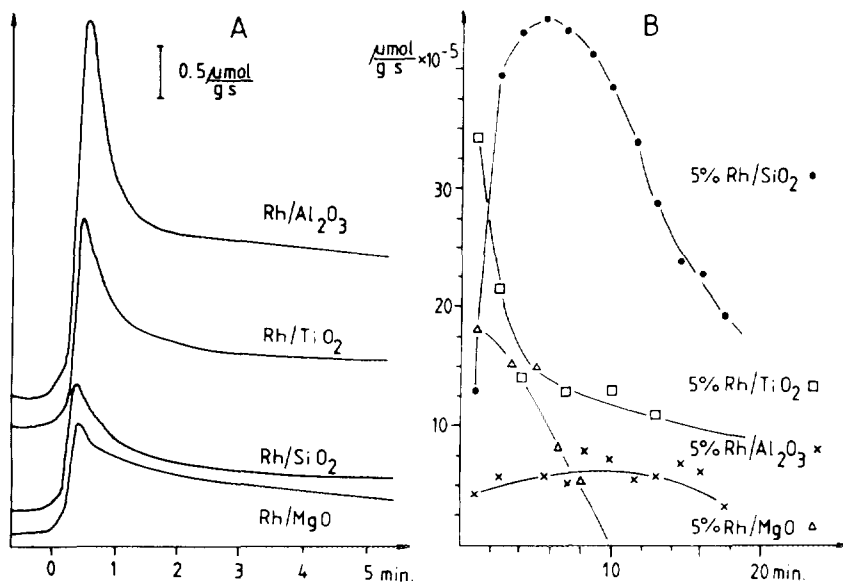


FIG. 2. Rates of H<sub>2</sub> (A) and C<sub>2</sub>H<sub>6</sub> (B) formation in the decomposition of CH<sub>4</sub> for supported Rh samples at 523 K (5% Rh/SiO<sub>2</sub> (●), 5% Rh/TiO<sub>2</sub> (□), 5% Rh/Al<sub>2</sub>O<sub>3</sub> (×), 5% Rh/MgO (△)). Flow rate of N<sub>2</sub> + CH<sub>4</sub> (12.5%): 40 ml/min. The amount of catalyst: 0.1g. In section (A), the curves are shifted.

exchange reaction with D<sub>2</sub> proceeds above 400 K on metal films (13, 14).

In the next experiments, the reactivity of the surface carbon formed in the decomposition was examined. This surface carbon exhibited a large variance with the conditions of its formation. Following its hydrogenation at the temperature of its formation (523 K), after flushing of the reactor with pure argon, a large amount of methane was produced initially on all the Rh samples, but this soon decayed to a low level. Ethane evolution was detected only on Rh/TiO<sub>2</sub>. Complete hydrogenation of the surface carbon was not reached at 523 K even after 1–2 h.

The existence of different forms of carbon on the surface is well illustrated by the TPR spectra in Fig. 3. When the surface carbon was produced at 423–523 K, a small proportion of it was hydrogenated to CH<sub>4</sub> even below 350–400 K. This reactive carbon is designated the α form. The majority of the surface carbon (β form) reacted at 400–550 K,  $T_p = 432$ –495 K. This was followed by

a high-temperature peak (for Rh/MgO and Rh/SiO<sub>2</sub>) above 550 K,  $T_p = 621$ –632 K (γ form). It appears that the support exerted a well-observable influence on the reactivity of the surface carbon. The relative amount of the more reactive forms was greater on Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/TiO<sub>2</sub> and less on Rh/SiO<sub>2</sub>.

The duration of formation of surface carbon at 523 K, i.e., the length of time for which the carbon was kept at this temperature, also influenced the distributions of carbon forms and of the hydrogenation products. At low contact time (1 min), with CH<sub>4</sub> at 523 K, higher hydrocarbons were also produced in addition to CH<sub>4</sub> on Rh/SiO<sub>2</sub> (0.15% C<sub>2</sub>H<sub>6</sub> and 0.03% C<sub>3</sub>H<sub>8</sub>). However, when the exposure time was extended to 10 min, only CH<sub>4</sub> was evolved.

When the Rh samples were exposed to CH<sub>4</sub> at higher temperatures, 673–773 K, the reactivity of the surface carbon was markedly decreased. The highly reactive α form was missing, and a significant proportion of the β carbon was transformed into a less reactive form, which reacted with H<sub>2</sub> above

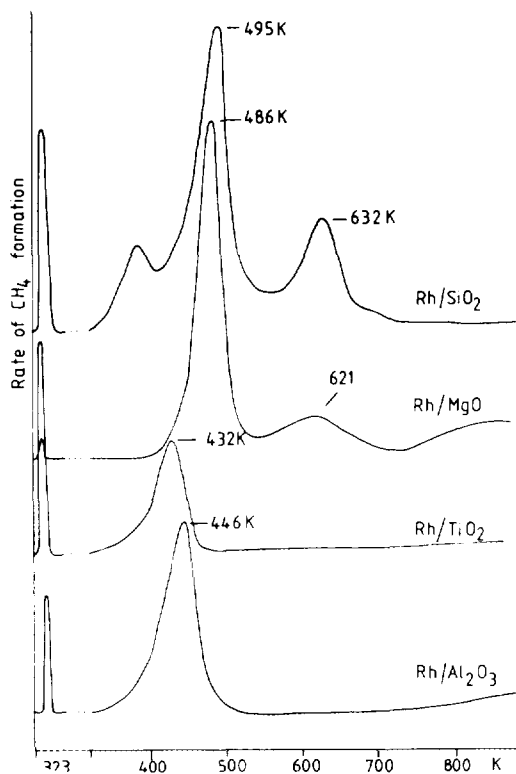


FIG. 3. Temperature-programmed reaction (TPR) of surface carbon with H<sub>2</sub> on supported Rh. Carbon was produced in the decomposition of pure CH<sub>4</sub> at 523 K for 1 min. The flow rate of CH<sub>4</sub>: 200 ml/min. The first peak was registered at 323 K under isotherm conditions.

720 K,  $T_{\max} = 878$  K (Fig. 4A). The reactivity towards O<sub>2</sub> and CO<sub>2</sub> of this rather inactive surface carbon is illustrated in the Fig. 4B. With O<sub>2</sub>, the reaction started above 400 K, but up to 570 K only a small amount of CO<sub>2</sub> was detected. The main CO<sub>2</sub> peak appeared at 745 K. CO<sub>2</sub> reacted with this carbon only above 550 K, and the reaction proceeded at higher rate above 700 K ( $T_{\max} = 963$  K).

### 3.2. Interaction of CO<sub>2</sub> with Rh

The most sensitive method for following the interaction of CO<sub>2</sub> with supported Rh and its dissociation on it is the IR spectroscopy, as CO, the primary product of this process, is strongly bonded to the Rh. In

agreement with previous measurements (15–18), CO<sub>2</sub> does not adsorb on Rh metals at and above room temperature, and no dissociation can be detected on supported Rh free of adsorbed hydrogen. However, the dissociation occurred at elevated temperatures (473–673 K, depending on the Rh content), as indicated by the appearance of a weak absorption band at 2020–2035 cm<sup>-1</sup> due to linearly bonded CO. The efficiency order of the supports was TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and SiO<sub>2</sub>. No gaseous CO was detected by mass spectrometry at these temperatures. This required much higher temperatures. In this case, however, the dissociation of CO also takes place, which is strongly influenced by the nature of the support (8).

### 3.3. CH<sub>4</sub> + CO<sub>2</sub> Surface Interaction

In the subsequent experiments we examined how the addition of CH<sub>4</sub> to CO<sub>2</sub> influences the dissociation of the CO<sub>2</sub>. Some selected spectra are displayed in Fig. 5. It is seen clearly that the band at 2030–2060 cm<sup>-1</sup> due to linearly bonded CO appears at lower temperatures and with higher intensities as compared with the CH<sub>4</sub>-free condition. There was no indication of the presence of dicarbonyl species or bridge-bonded CO. The position of the CO band was practically the same as observed in the presence of pure CO<sub>2</sub>.

Some measurements were also performed under the dynamic conditions used for study of the adsorption and dissociation of CH<sub>4</sub>. In the CH stretching frequency region, we could not register any spectral features, similarly as in the absence of CO<sub>2</sub>.

### 3.4. Reactions of CH<sub>4</sub> with CO<sub>2</sub>

The reaction was first investigated in the low-temperature range, 423–573 K, where we observed an initial C<sub>2</sub>H<sub>6</sub> formation and CH<sub>4</sub> decomposition. Addition of a small amount of CO<sub>2</sub> (4% of CH<sub>4</sub>) to the CH<sub>4</sub> already resulted in a decrease in the production of C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub>, and led to the generation of CO. This was more pronounced at higher CO<sub>2</sub> content (Fig. 6).

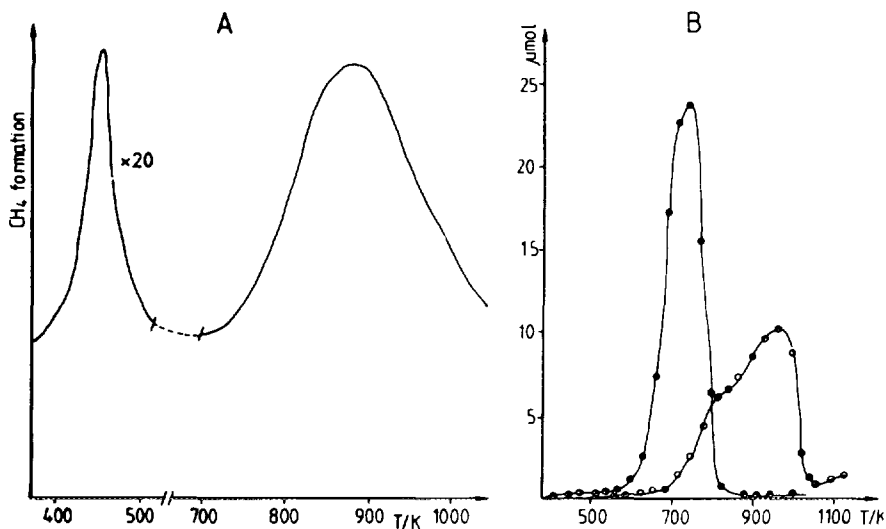


FIG. 4. Temperature programmed reaction (TPR) spectra of surface carbon on 1% Rh/Al<sub>2</sub>O<sub>3</sub> with H<sub>2</sub> (A) and with O<sub>2</sub> (●), which produced CO<sub>2</sub>, and with CO<sub>2</sub> (○), which gave CO (B). Carbon was produced in the decomposition of CH<sub>4</sub> at 773 K, the flow rate of CH<sub>4</sub> was 200 ml/min and the amount of catalyst was 0.3 g.

With increase of the temperature, the rates of CO and H<sub>2</sub> formation increased. More detailed measurements were performed at 673–773 K. In this temperature range, C<sub>2</sub> hydrocarbons were detected only in traces. Zero or only slight deactivation of the catalyst samples occurred during the conditioning period at 773 K. The CO/H<sub>2</sub> ratio varied little during the reaction. The highest value was obtained for Rh/Al<sub>2</sub>O<sub>3</sub> (Table 1).

After the 1-h reaction at 773 K, we found only a relatively small amount of carbon on all the samples. The carbon was determined in the form of CO<sub>2</sub> by treating the catalysts with O<sub>2</sub> at 773 and 873 K. The highest value was obtained for Rh/Al<sub>2</sub>O<sub>3</sub>, but even in this case Rh<sub>surf</sub>/C was only 0.07. On Rh/TiO<sub>2</sub> only traces of CO<sub>2</sub> were detected. The data are presented in Table 1.

We studied the effect of the reactant concentration on the rate of product formation. With the increase of the CH<sub>4</sub> concentration, the formation of CO and H<sub>2</sub> increased (Fig. 7). The dependence of the product formation rate on the concentration of CO<sub>2</sub> was

more complicated. The CO formation increased, but the H<sub>2</sub> production rate exhibited a maximum on all samples with the increase of the CO<sub>2</sub> content. The kinetic orders were calculated from the logarithmic plots of the various rates versus the volume percentage of the reactant of interest (Fig. 7, Table 2). On different supported Rh samples, the order with respect to CH<sub>4</sub> was 0.33–0.22, and was 0.18–0.38 for the formation of CO and H<sub>2</sub>, respectively. The order with respect to CO<sub>2</sub> was 0.34–0.43 for CO formation. It was 0.2–0.38 for H<sub>2</sub> on all samples up to 20%. Above this concentration range, with the exception of Rh/SiO<sub>2</sub>, the order was negative (Table 2). From the temperature dependence of the formation of H<sub>2</sub> and CO, the apparent activation energies were determined (Fig. 8). We always obtained somewhat higher values for the production of H<sub>2</sub> than for that of CO (Table 2); as a result, a slight decrease in the CO/H<sub>2</sub> ratio occurred with increase of temperature.

In order to compare the efficiencies of the supports, we calculated the turnover frequency, and the rates of H<sub>2</sub> and CO formation

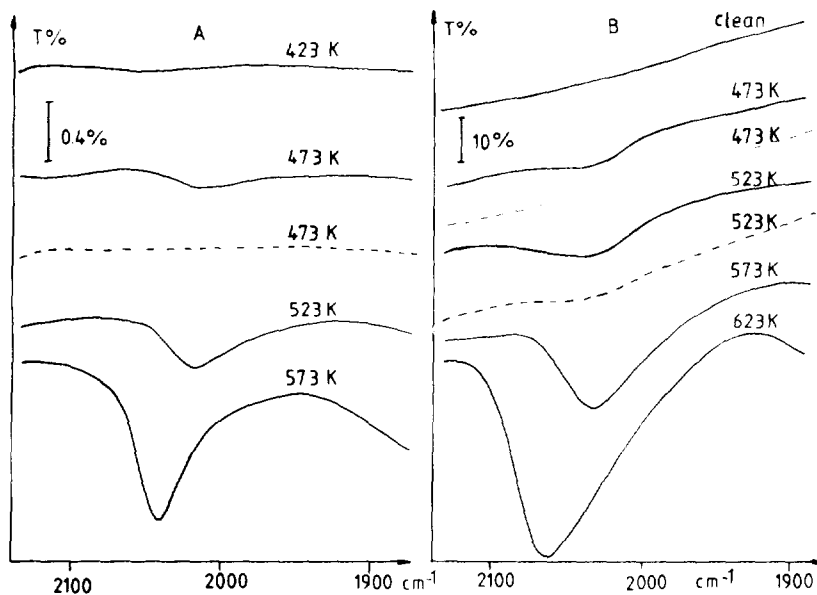


FIG. 5. Infrared spectra of supported Rh following 50 Torr of CO<sub>2</sub> + CH<sub>4</sub> (1 : 1) adsorption at different temperatures. Spectra were always taken at 300 K. For comparison we present spectra obtained in the presence of CO<sub>2</sub> alone (dotted line): (A) Rh/SiO<sub>2</sub> and (B) Rh/Al<sub>2</sub>O<sub>3</sub>.

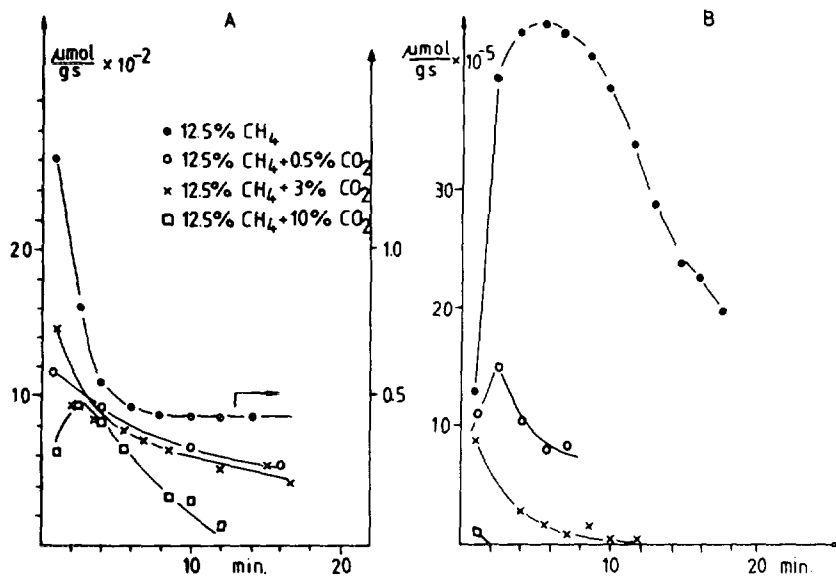


FIG. 6. Effects of CO<sub>2</sub> concentration on the decomposition of CH<sub>4</sub> on Rh/SiO<sub>2</sub> at 523 K. The flow rate: 40 ml/min. The amount of catalyst: 0.1g. H<sub>2</sub> (A) and C<sub>2</sub>H<sub>6</sub> (B).

TABLE I

Some Characteristic Data for the  $\text{CO}_2 + \text{CH}_4$  Reaction on Supported Rh Catalysts at 773 K

D (%)	Conversion		Formation rate				CO/H <sub>2</sub>	Surface carbon <sup>a</sup> C/Rh	
	CO <sub>2</sub> (%)	CH <sub>4</sub> (%)	CO	TOF <sup>b</sup> (s <sup>-1</sup> )	H <sub>2</sub>	TOF <sup>b</sup> (s <sup>-1</sup> )			
									$\frac{\mu\text{mol}}{\text{g} \cdot \text{s}}$
1% Rh/TiO <sub>2</sub>	30.4	11.5 ± 0.02	18.7 ± 0.11	11.0	0.37	6.5	0.22	1.68	0.003
1% Rh/Al <sub>2</sub> O <sub>3</sub>	46.2	11.6 ± 0.07	21.7 ± 0.26	17.5	0.39	6.7	0.15	2.62	0.06
1% Rh/MgO	11.9	10.4 ± 0.16	16.8 ± 0.27	9.8	0.85	5.8	0.5	1.68	0.04
1% Rh/SiO <sub>2</sub>	41.5	13.8 ± 0.12	21.2 ± 0.10	13.1	0.32	8.1	0.2	1.63	0.04

<sup>a</sup> The amount of surface carbon formed in the first hour of the reaction. The carbon was determined in the form of CO<sub>2</sub> by treating the surface with O<sub>2</sub> at 773 and 873 K.

<sup>b</sup> Turnover frequency; rates related to the number of surface metal atoms.

relative to the number of surface Rh atoms. The highest specific activities were obtained for Rh/MgO. For the other samples these values were almost the same. Note that the supports alone were completely inactive for this reaction up to 823 K.

#### 4. DISCUSSION

Let us first consider the dissociation of CH<sub>4</sub> and CO<sub>2</sub> on supported Rh catalysts.

#### 4.1. Dissociation of CH<sub>4</sub>

The adsorption and dissociation of CH<sub>4</sub> has previously been investigated on Rh films (14) and a Rh single-crystal surface (19). Although the initial sticking coefficient for methane chemisorption in the temperature range below the critical temperature was the lowest for Rh film (among Cu, Ag, Pd, Re, Ni, Mo, W, Ta, and Ti), it was almost the most active in the decomposition of methane. The

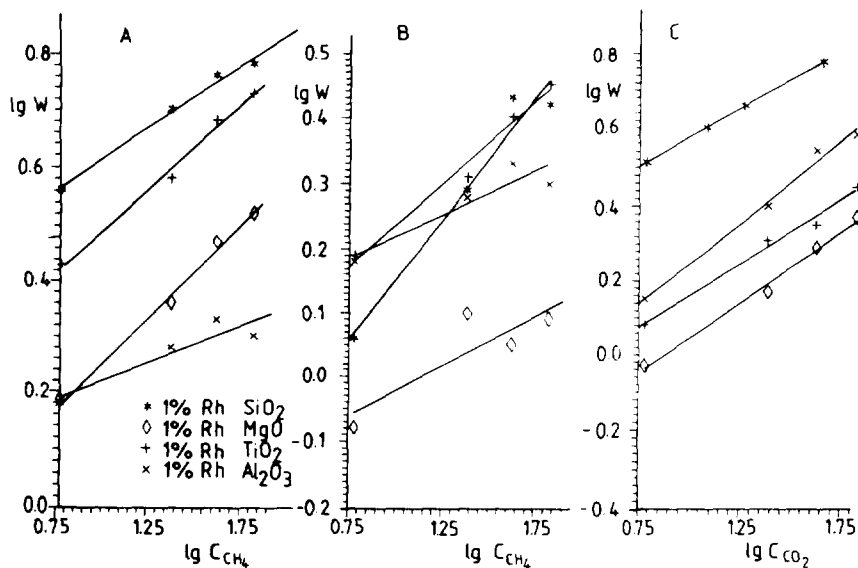


FIG. 7. Dependence of the rate of product formation in  $\text{CH}_4 + \text{CO}_2$  reaction on the partial pressure of  $\text{CH}_4$  and  $\text{CO}_2$  at 773 K. (A) and (C), formation of CO; (B) formation of H<sub>2</sub>.



TABLE 2

Some Kinetic Data for the CO<sub>2</sub> + CH<sub>4</sub> Reaction on Supported Rh Catalysts at 773 K

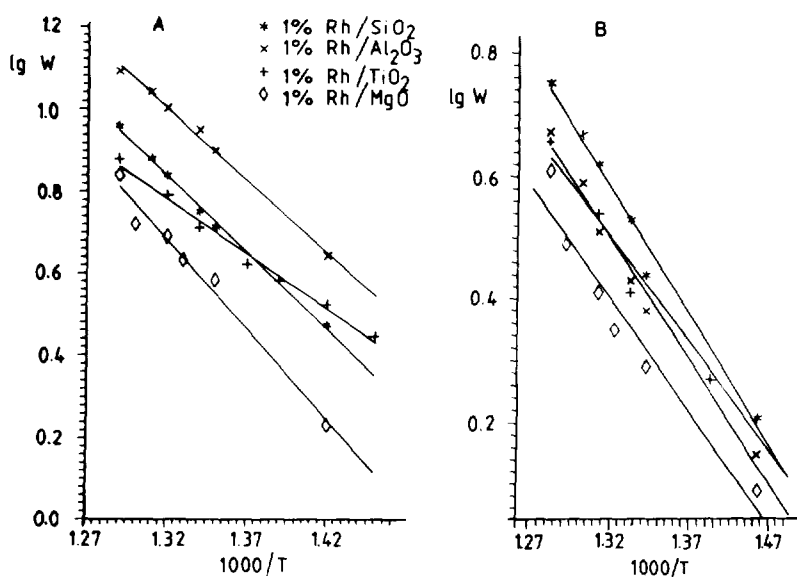
	$E_{\text{CO}}$ (kcal/mol)	$E_{\text{CH}_4}$ (kcal/mol)	Kinetic order				
			CH <sub>4</sub>		CO <sub>2</sub>		
			CO	H <sub>2</sub>	CO	H <sub>2</sub>	
					a	b	
1% Rh/TiO <sub>2</sub>	12.4	15.8	0.29	0.24	0.34	0.2	-0.89
1% Rh/Al <sub>2</sub> O <sub>3</sub>	16.0	18.2	0.22	0.14	0.43	0.29	-0.6
1% Rh/MgO	20.3	23.2	0.33	0.16	0.38	0.38	-1.0
1% Rh/SiO <sub>2</sub>	17.2	19.1	0.22	0.38	0.23	0.31	0.31

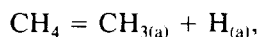
Note.  $E_{\text{CO}}$  and  $E_{\text{H}_2}$ , activation energies for CO and H<sub>2</sub> formation. a. The order up to 20% CO<sub>2</sub> content; b. the order above 20% CO<sub>2</sub> content.

temperature at which hydrogen evolution started on Rh film was 323 K at a pressure of  $2 \times 10^{-2}$  Torr of methane (14). From a quantitative study of the CH<sub>4</sub>-H<sub>2</sub> equilibrium, the average composition of the hydrocarbon fragments on the Rh surface was calculated to be H/C = 1 at high hydrocarbon coverages (14). Rh film also exhibited high activity in catalyzing the exchange of methane with deuterium. The reaction occurred only in the

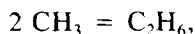
temperature range where the chemisorption of CH<sub>4</sub> took place with H<sub>2</sub> evolution (13, 14). The exchange reaction was also studied on 0.5% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst at 593 K, where it occurred quite rapidly (20).

In the present work, the dissociation of CH<sub>4</sub> in a flow system on supported Rh was found above 423 K, when C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> were identified. The primary step is undoubtedly the formation of CH<sub>3</sub>,

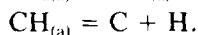
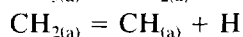
FIG. 8. Arrhenius diagrams for CO (A) and H<sub>2</sub> (B) formation in the CH<sub>4</sub> + CO<sub>2</sub> reaction.



which may dimerize to give  $\text{C}_2\text{H}_6$ ,



and also decompose further:



Although, the formation of  $\text{C}_2\text{H}_6$  was observed on all samples in the initial stage of the interaction of  $\text{CH}_4$  with Rh catalyst, we did not succeed in identifying any adsorbed  $\text{CH}_3$  or  $\text{CH}_x$  fragments by means of sensitive FTIR measurements. This suggests that the lifetimes of the  $\text{CH}_3$  and  $\text{CH}_x$  species are very short at the temperature of the reaction, and/or their concentrations are below the detection limit. A similar conclusion was reached for other silica-supported Pt metals (1). The larger amount of  $\text{H}_2$  obtained compared with that of  $\text{C}_2\text{H}_6$  indicated that the further dissociation of  $\text{CH}_3$  and its complete decomposition occurred in parallel with the dimerization of  $\text{CH}_3$ . This process continued for a while even after termination of the formation of  $\text{C}_2\text{H}_6$ . It is most likely that the surface carbon formed soon blocked the active areas of the metal, and the decomposition of  $\text{CH}_4$  ceased.

The dimerization of adsorbed  $\text{CH}_2$  and  $\text{CH}$  species seemed to occur to a very small extent, as there was no indication of the formation of either  $\text{C}_2\text{H}_4$  or  $\text{C}_2\text{H}_2$ . Pd/SiO<sub>2</sub> is an exception in this respect as the formation of  $\text{C}_2\text{H}_4$  was observed besides of  $\text{C}_2\text{H}_6$  (1).

From the data presented in Fig. 2, it appears clearly that the support exerts a significant influence on the activation of  $\text{CH}_4$  and on the further reactions of adsorbed  $\text{CH}_3$  species. As regards the decomposition of  $\text{CH}_4$ , taking into account the dispersity of the Rh samples, the most effective catalyst was Rh/Al<sub>2</sub>O<sub>3</sub>. This was followed by Rh/TiO<sub>2</sub>, Rh/MgO, and Rh/SiO<sub>2</sub>. The amounts of  $\text{C}_2\text{H}_6$  measured decreased in this sequence. Although it cannot be excluded

that the activation of methane on Rh may be affected by the nature of the interaction between the support and the Rh (21), which strongly influenced the specific rates of hydrogenation of CO and CO<sub>2</sub> on the same Rh samples (7), we believe that the differences in the present case are mainly associated with the differences in crystal size of the Rh, and/or with the ease of carbon migration from the Rh to the support, producing a free Rh surface on the catalyst. This may be in agreement with the observation that no significant support effect was registered in the high-temperature reaction of  $\text{CH}_4$  and CO<sub>2</sub>, where only a minor amount of carbon was deposited on the catalyst surface.

The reaction of surface carbon was investigated in great detail, as the decomposition of  $\text{CH}_4$  and the hydrogenation of surface carbon to higher hydrocarbons have recently been proposed as a possible mode of transformation of  $\text{CH}_4$  into more valuable compounds (3, 22). The reactivity of surface carbon towards hydrogen, studied by TPR spectroscopy, exhibited practically the same features as established in our former work, when carbon was produced by the dissociation of CO (8). Accordingly, oxygen, the coadsorbed species, exerts only a slight influence on the reactivity of surface carbon. We can distinguish three forms of carbon: (i) the highly reactive carbidic form ( $\alpha$ ), which can be hydrogenated even below 350–400 K, (ii) a less reactive amorphous layer ( $\beta$ ),  $T_p = 235$ –495 K, and (iii) the relatively inactive graphitic form ( $\gamma$ ), which reacts with hydrogen only above 650 K. This has been also observed in subsequent studies (23).

An interesting feature is that the reactivity of the surface carbon is very sensitive to the temperature of its formation, and also to the duration of its thermal treatment. Above 573 K, a significant aging was observed, with the transformation of the more reactive form into less reactive ones. This behavior was exhibited in the products of hydrogenation of the surface carbon, too. When the time of exposure to  $\text{CH}_4$  was kept short at 523 K

(1 min), or the carbon was produced at 473 K, a detectable amount of higher hydrocarbons was produced on Rh/SiO<sub>2</sub>. The formation of higher hydrocarbons in this reaction up to C<sub>6</sub>, has also been observed on Pt/SiO<sub>2</sub> (EUROPRT 1) (3) and on SiO<sub>2</sub> supported Pt metal catalysts (1).

#### 4.2. Dissociation of CO<sub>2</sub>

The question of the dissociation of CO<sub>2</sub> on Rh has been the subject of great controversy in the literature. Results and different views are summarized in a recent review (24).

The dissociation of CO<sub>2</sub> on the samples used in the present study was followed by IR spectroscopy. In harmony with previous measurements (15–18), a weak CO band absorbing at 2020–2035 cm<sup>-1</sup> was detected only at and above 573 K. An interesting feature of the interaction of CO<sub>2</sub> with supported Rh is that only linearly bonded CO was produced, while the adsorption of CO alone on the same Rh samples gave mainly the dicarbonyl species Rh<sup>+</sup>(CO)<sub>2</sub>. Recent EXAFS (25) and IR spectroscopic measurements (26–28) revealed that, because of the CO-induced disruption of Rh clusters, Rh<sub>x</sub>-CO species can be transformed into Rh<sup>+</sup>(CO)<sub>2</sub> at 150–423 K. At higher temperatures the reverse process, the reformation of Rh<sub>x</sub>-CO from Rh<sup>+</sup>(CO)<sub>2</sub>, predominates. In the present case this oxidative disruption of Rh clusters was not observed, very probably because of the very small concentration of adsorbed CO.

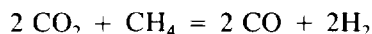
#### 4.3. CH<sub>4</sub> + CO<sub>2</sub> Interaction

When CH<sub>4</sub> was added to the CO<sub>2</sub>, the temperature of CO formation both on the catalyst surface and in the gas phase was greatly decreased. In this case the absorption band due to linearly bonded CO was detected even at 473 K. This means that the hydrogen formed in the CH<sub>4</sub> decomposition promoted the dissociation of CO<sub>2</sub>. This is consistent with the previous findings that hydrogen can greatly facilitate this process (15–17).

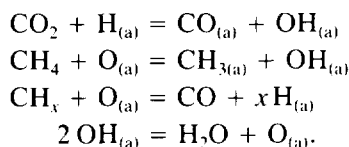
#### 4.4. Catalytic Reaction between CH<sub>4</sub> and CO<sub>2</sub>

Although great attention is being paid to the conversion of CO<sub>2</sub> and CH<sub>4</sub> to more valuable compounds, few papers have dealt with the catalytic reaction between CO<sub>2</sub> and CH<sub>4</sub> (2, 4, 29–33), which is commercialized as the Calcor process (29).

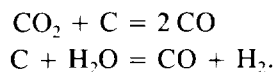
On the Rh samples used in the present study, the CH<sub>4</sub> + CO<sub>2</sub> reaction



proceeded with high conversion 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 rhodium 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 CO<sub>2</sub> by hydrogen, and perhaps by CH<sub>x</sub> fragments, too, the decomposition products of CH<sub>4</sub>, and (ii) facilitation of the dissociation of CH<sub>4</sub> by adsorbed O formed in the decomposition of CO<sub>2</sub>, which may activate the CH<sub>4</sub> molecule. Accordingly, besides to the steps postulated for the decomposition of the reactants, we may count with the following reactions:



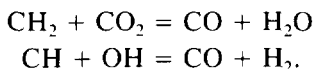
The carbon formed in the dissociation of CH<sub>4</sub> may react either with CO<sub>2</sub>, as demonstrated by the results in Fig. 4, or with H<sub>2</sub>O,



As the aging of carbon (formed in the dissociation of either CO (8) or CH<sub>4</sub>) at high temperature is fast, which leads to transformation of the surface carbon into a less reactive amorphous form, deposition of a significant amount of unreactive surface carbon on the

catalyst surface was expected. However, this was not the case, which means that the removal of surface carbon is very efficient in these steps. In agreement with this, no deactivation of the Rh catalysts was experienced. Nor was carbon deposition on supported Rh observed by Richardson and Paripatyadar (4) during a much longer run under industrial conditions. Accordingly, the carbon (we may call it "status nascendi") formed in the CH<sub>4</sub> dissociation interacts with CO<sub>2</sub> and H<sub>2</sub>O immediately after its production, before the aging process commences.

However, it cannot be excluded that, before their complete dissociation, the CH<sub>x</sub> fragments react with CO<sub>2</sub> and H<sub>2</sub>O, for instance,



Although we cannot decide between the two alternatives, at this stage of our work, it is most likely that all the reactions occur simultaneously.

The facts that the ratio CO/H<sub>2</sub> was always higher than 1, and varied with the temperature and the catalyst, indicate the occurrence of several secondary processes in this complex system, e.g., the hydrogenation of CO, CO<sub>2</sub> and water-gas shift reaction. The reported maximum in the H<sub>2</sub> formation rate with increasing CO<sub>2</sub> concentration may be attributed to the latter process.

It is an interesting feature of the high-temperature CH<sub>4</sub> + CO<sub>2</sub> reaction on Rh catalysts that the rates of CH<sub>4</sub> conversion and product formation hardly depend on the nature of the support. This is in complete contrast with the results obtained on the hydrogenation of CO (5) and of CO<sub>2</sub> (7) and on the NO + CO reaction (34) on the same catalysts prepared in our laboratory. In these reactions, the specific activity of Rh/TiO<sub>2</sub> exceeded that of the less active Rh/MgO and Rh/SiO<sub>2</sub> by almost two orders of magnitude. As the support also exerted a significant influence on the dissociation of CO<sub>2</sub> (Rh/TiO<sub>2</sub> was the most active and Rh/

SiO<sub>2</sub> the least active), it may be concluded that the activation and dissociation of CO<sub>2</sub> do not play an important role in the CH<sub>4</sub> + CO<sub>2</sub> reaction over Rh. In other words, the dissociation of CH<sub>4</sub> and the presence of hydrogen diminish the difference in the effect of the support on the dissociation of CO<sub>2</sub> on Rh.

#### CONCLUSION

(i) Supported Rh was found to be active in the decomposition of CH<sub>4</sub> to give hydrogen, a smaller amount of ethane, and carbonaceous residues. The activity order was Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/TiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Rh/MgO. (ii) By means of TPR at least three different kinds of surface carbon were distinguished. The hydrogenation of the most reactive one produced higher hydrocarbons. (iii) Addition of CH<sub>4</sub> to CO<sub>2</sub>, or vice versa, promotes the dissociation of other compounds. (iv) Supported Rh is active in the high-temperature reaction of CO<sub>2</sub> + CH<sub>4</sub> to give H<sub>2</sub> and CO without carbon deposition.

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