

Activation of CH₄ and Its Reaction with CO₂ 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*¹

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The dissociation of CH₄ and CO₂, as well as the reaction between CH₄ and CO₂, 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 CO₂ was detected by infrared spectroscopy only above 523 K, and it was promoted by the presence of CH₄. The reaction between CO₂ and CH₄ proceeded rapidly above 673 K to give CO and H₂ 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 CH₄ (1) and in the CH₄ + CO₂ reaction (2). In the first case we observed C₂H₆ and H₂ 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 CH₄ and higher hydrocarbons. Because of the accumulation of carbon, the ability of the catalyst to activate CH₄ decreased to almost zero in 10–15 min. As regards the decomposition of CH₄, the most active metal was Ru/SiO₂, whereas the highest amount of C₂H₆ was produced on Pt/SiO₂. The ability of Pt/SiO₂ to produce C₂H₆ in the decomposition of CH₄ has been also observed by Belgued *et al.* (3).

Supported Pt metals exhibited high activ-

ity in the CH₄ + CO₂ reaction, to give CO, H₂, and a small amount of C₂H₆ 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 CH₄ 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/Al₂O₃ in the CO₂ 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 CO₂ (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 H₂ to give

¹ 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: Al_2O_3 , (Degussa), TiO_2 (Degussa P25), SiO_2 (Cab-O-Sil), and 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 10×30 -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 N_2 for 15 min.

The gases used were initially commercial purity. The CO_2 was further purified by fractional distillation. He (99.995 %) and 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 h^{-1} . The exit gases were analyzed gas chromatographically (Hewlett-Packard 5890 and 5710) on Porapak QS column. The CO , CO_2 , and CH_4 were determined in the He carrier gas, and H_2 was detected simultaneously in the N_2 stream by a thermal conductivity detector. The conversion of CO_2 and CH_4 were defined as the converted CO_2 or CH_4 per the total amount of CO_2 or 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 H_2 , the sample was heated at 12 K min^{-1} , and the hydrocarbons formed were analyzed (8).

The decomposition of 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 N_2 , the temperature of the catalyst was lowered to the reaction temperature and then the N_2 stream was switched to N_2 containing 12.5% CH_4 . The amount of 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 H_2 - O_2 titration at 298 K using the pulse technique (5, 7).

3. RESULTS

3.1. Interaction of CH_4 with Rh

The interaction of CH_4 with supported Rh was studied first in a flow system by analyzing the products formed. The evolution of C_2H_6 and H_2 was registered on every Rh sample. The amount of H_2 was always higher than that of C_2H_6 . The initial rate of CH_4 decomposition was very high, but it decayed quickly to a very low value. More detailed measurements were performed on Rh/ 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

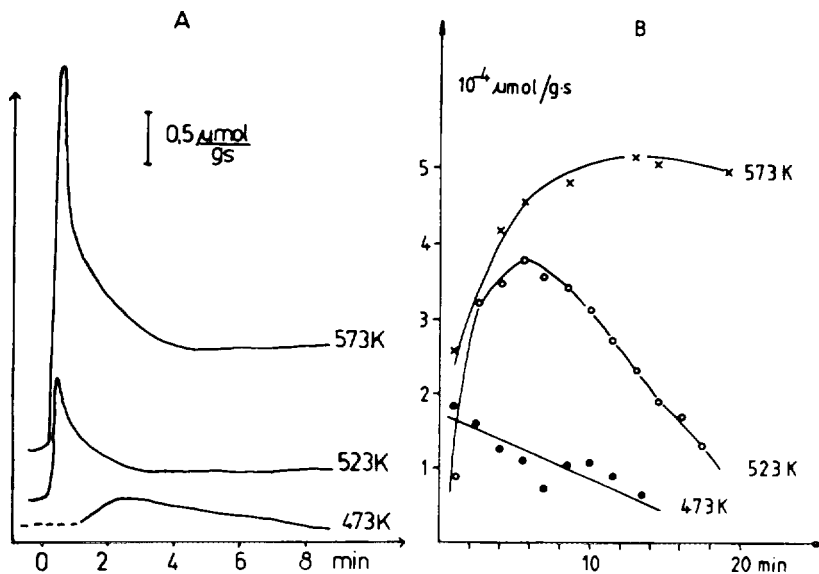


FIG. 1. Effects of temperature on the rates of H₂ (A) and C₂H₆ (B) formation on 5% Rh/SiO₂. Flow rate of N₂ + CH₄ (12.5%): 40 ml/min. The amount of catalyst: 0.1g.

product formation increased, but the C₂H₆/H₂ 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 CH₄ and the product distribution are influenced by the nature of the support. The most effective catalyst for the H₂ formation was the Rh/Al₂O₃, which was followed by Rh/TiO₂, Rh/SiO₂, and Rh/MgO, but the highest C₂H₆ formation was observed on Rh/SiO₂. The decomposition of CH₄ at the maximum of H₂ evolution was 44.3% for Rh/Al₂O₃, 25.4% for Rh/TiO₂, 19.2% for Rh/SiO₂, and 15.6% for Rh/MgO.

It is important to mention that no reaction of CH₄ occurred on the supports alone.

The large excess of hydrogen produced in the interaction of CH₄ with supported Rh indicated the partial or full decomposition of CH₄ to CH_x 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 CH₄ or with CH₄ + N₂ gas mixture, and the spectrum was registered again at 200 K. Afterwards the wafer was lifted into a CH₄-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 CH₄. The gas-phase spectrum of CH₄ 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_x 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⁻¹, where absorption bands due to adsorbed CH₃ species have been readily detected following the dissociation of CH₃I on single-crystal surfaces (9–11) and on Pd/SiO₂ (12). Our failure to detect the transitory species of CH₄ dissociation is disappointing if we consider that the

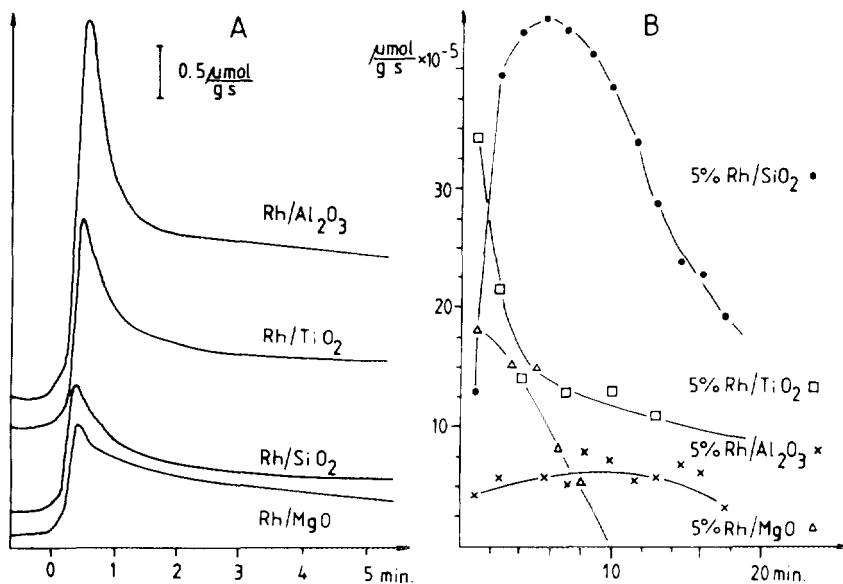


FIG. 2. Rates of H₂ (A) and C₂H₆ (B) formation in the decomposition of CH₄ for supported Rh samples at 523 K (5% Rh/SiO₂ (●), 5% Rh/TiO₂ (□), 5% Rh/Al₂O₃ (×), 5% Rh/MgO (△)). Flow rate of N₂ + CH₄ (12.5%): 40 ml/min. The amount of catalyst: 0.1g. In section (A), the curves are shifted.

exchange reaction with D₂ 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/TiO₂. 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 CH₄ 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/SiO₂) 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/Al₂O₃ and Rh/TiO₂ and less on Rh/SiO₂.

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 CH₄ at 523 K, higher hydrocarbons were also produced in addition to CH₄ on Rh/SiO₂ (0.15% C₂H₆ and 0.03% C₃H₈). However, when the exposure time was extended to 10 min, only CH₄ was evolved.

When the Rh samples were exposed to CH₄ 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 H₂ above

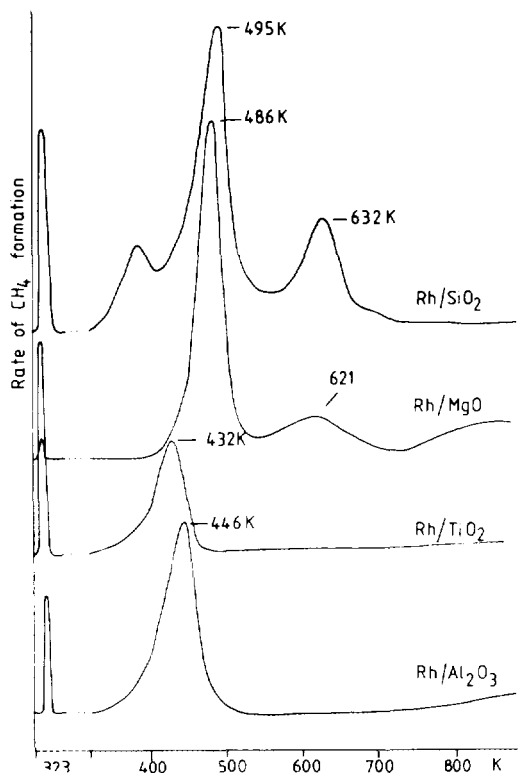


FIG. 3. Temperature-programmed reaction (TPR) of surface carbon with H₂ on supported Rh. Carbon was produced in the decomposition of pure CH₄ at 523 K for 1 min. The flow rate of CH₄: 200 ml/min. The first peak was registered at 323 K under isotherm conditions.

720 K, $T_{\max} = 878$ K (Fig. 4A). The reactivity towards O₂ and CO₂ of this rather inactive surface carbon is illustrated in the Fig. 4B. With O₂, the reaction started above 400 K, but up to 570 K only a small amount of CO₂ was detected. The main CO₂ peak appeared at 745 K. CO₂ 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 CO₂ with Rh

The most sensitive method for following the interaction of CO₂ 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), CO₂ 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⁻¹ due to linearly bonded CO. The efficiency order of the supports was TiO₂, Al₂O₃, MgO, and SiO₂. 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. CH₄ + CO₂ Surface Interaction

In the subsequent experiments we examined how the addition of CH₄ to CO₂ influences the dissociation of the CO₂. Some selected spectra are displayed in Fig. 5. It is seen clearly that the band at 2030–2060 cm⁻¹ due to linearly bonded CO appears at lower temperatures and with higher intensities as compared with the CH₄-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 CO₂.

Some measurements were also performed under the dynamic conditions used for study of the adsorption and dissociation of CH₄. In the CH stretching frequency region, we could not register any spectral features, similarly as in the absence of CO₂.

3.4. Reactions of CH₄ with CO₂

The reaction was first investigated in the low-temperature range, 423–573 K, where we observed an initial C₂H₆ formation and CH₄ decomposition. Addition of a small amount of CO₂ (4% of CH₄) to the CH₄ already resulted in a decrease in the production of C₂H₆ and H₂, and led to the generation of CO. This was more pronounced at higher CO₂ content (Fig. 6).

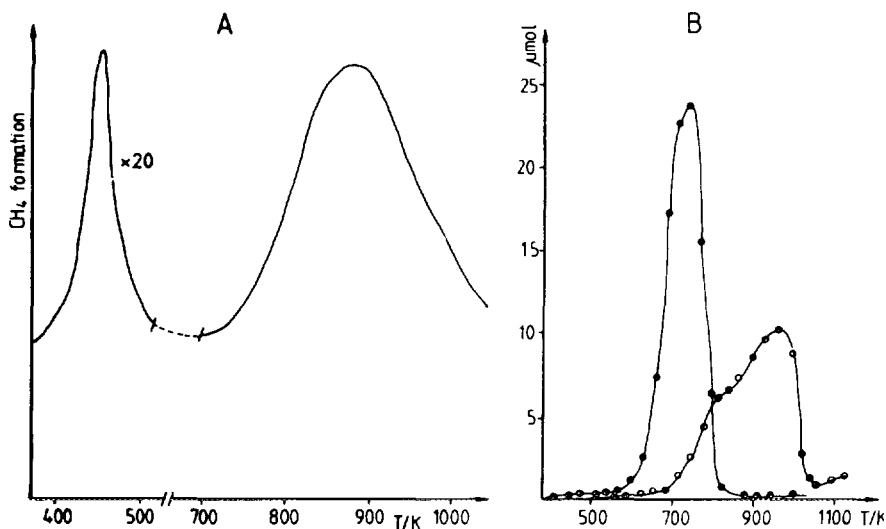


FIG. 4. Temperature programmed reaction (TPR) spectra of surface carbon on 1% Rh/Al₂O₃ with H₂ (A) and with O₂ (●), which produced CO₂, and with CO₂ (○), which gave CO (B). Carbon was produced in the decomposition of CH₄ at 773 K, the flow rate of CH₄ was 200 ml/min and the amount of catalyst was 0.3 g.

With increase of the temperature, the rates of CO and H₂ formation increased. More detailed measurements were performed at 673–773 K. In this temperature range, C₂ 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/H₂ ratio varied little during the reaction. The highest value was obtained for Rh/Al₂O₃ (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 CO₂ by treating the catalysts with O₂ at 773 and 873 K. The highest value was obtained for Rh/Al₂O₃, but even in this case Rh_{surf}/C was only 0.07. On Rh/TiO₂ only traces of CO₂ 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 CH₄ concentration, the formation of CO and H₂ increased (Fig. 7). The dependence of the product formation rate on the concentration of CO₂ was

more complicated. The CO formation increased, but the H₂ production rate exhibited a maximum on all samples with the increase of the CO₂ 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 CH₄ was 0.33–0.22, and was 0.18–0.38 for the formation of CO and H₂, respectively. The order with respect to CO₂ was 0.34–0.43 for CO formation. It was 0.2–0.38 for H₂ on all samples up to 20%. Above this concentration range, with the exception of Rh/SiO₂, the order was negative (Table 2). From the temperature dependence of the formation of H₂ and CO, the apparent activation energies were determined (Fig. 8). We always obtained somewhat higher values for the production of H₂ than for that of CO (Table 2); as a result, a slight decrease in the CO/H₂ ratio occurred with increase of temperature.

In order to compare the efficiencies of the supports, we calculated the turnover frequency, and the rates of H₂ and CO formation

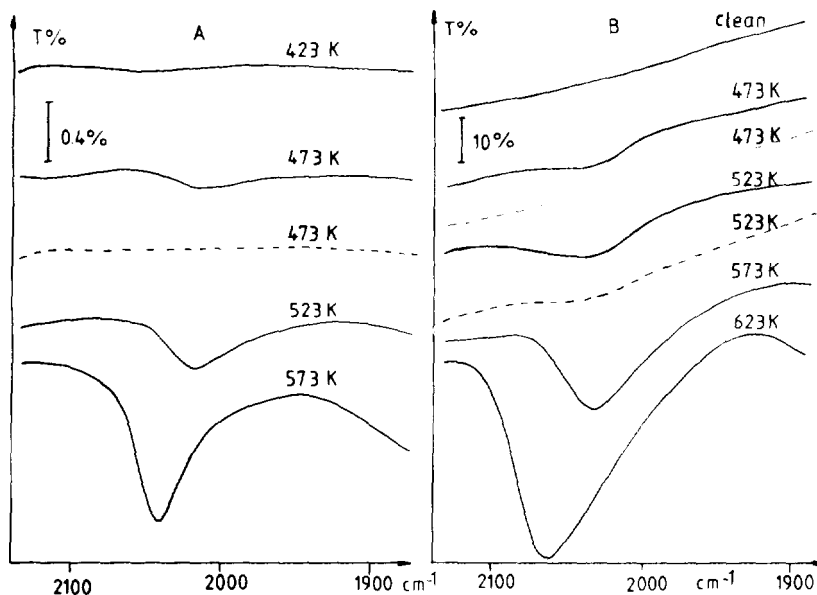


FIG. 5. Infrared spectra of supported Rh following 50 Torr of CO₂ + CH₄ (1 : 1) adsorption at different temperatures. Spectra were always taken at 300 K. For comparison we present spectra obtained in the presence of CO₂ alone (dotted line): (A) Rh/SiO₂ and (B) Rh/Al₂O₃.

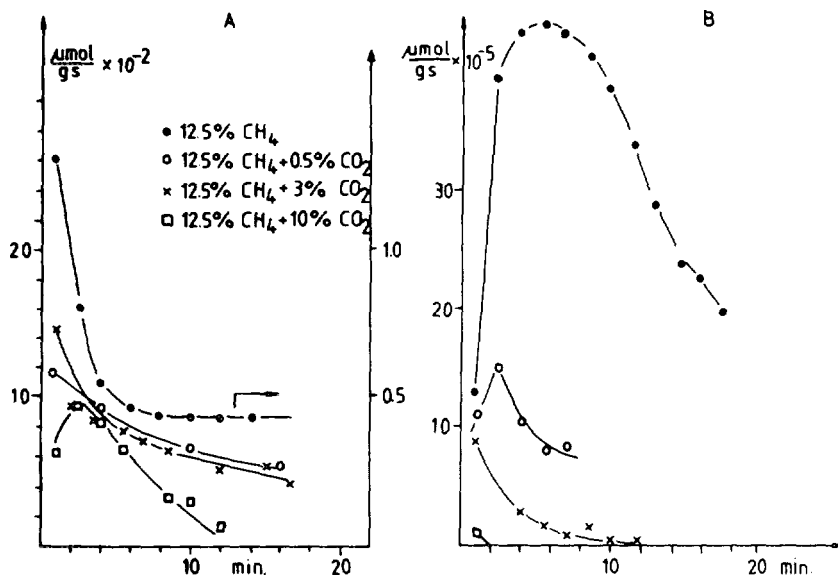


FIG. 6. Effects of CO₂ concentration on the decomposition of CH₄ on Rh/SiO₂ at 523 K. The flow rate: 40 ml/min. The amount of catalyst: 0.1g. H₂ (A) and C₂H₆ (B).

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 ₂	Surface carbon ^a C/Rh	
	CO ₂ (%)	CH ₄ (%)	CO	TOF ^b (s ⁻¹)	H ₂	TOF ^b (s ⁻¹)			
									$\frac{\mu\text{mol}}{\text{g} \cdot \text{s}}$
1% Rh/TiO ₂	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 ₂ O ₃	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 ₂	41.5	13.8 ± 0.12	21.2 ± 0.10	13.1	0.32	8.1	0.2	1.63	0.04

^a The amount of surface carbon formed in the first hour of the reaction. The carbon was determined in the form of CO₂ by treating the surface with O₂ at 773 and 873 K.

^b 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 CH₄ and CO₂ on supported Rh catalysts.

4.1. Dissociation of CH₄

The adsorption and dissociation of CH₄ 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

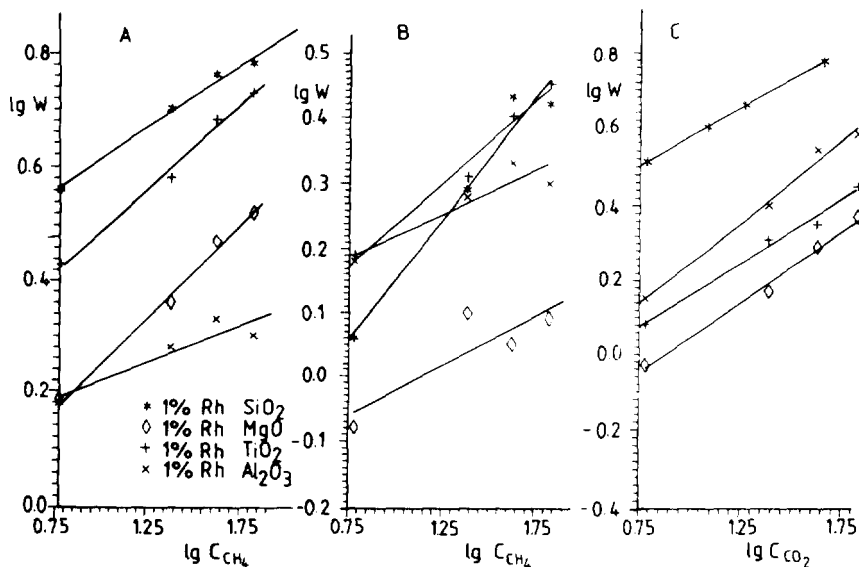


FIG. 7. Dependence of the rate of product formation in CH₄ + CO₂ reaction on the partial pressure of CH₄ and CO₂ at 773 K. (A) and (C), formation of CO; (B) formation of H₂.

TABLE 2

Some Kinetic Data for the CO₂ + CH₄ Reaction on Supported Rh Catalysts at 773 K

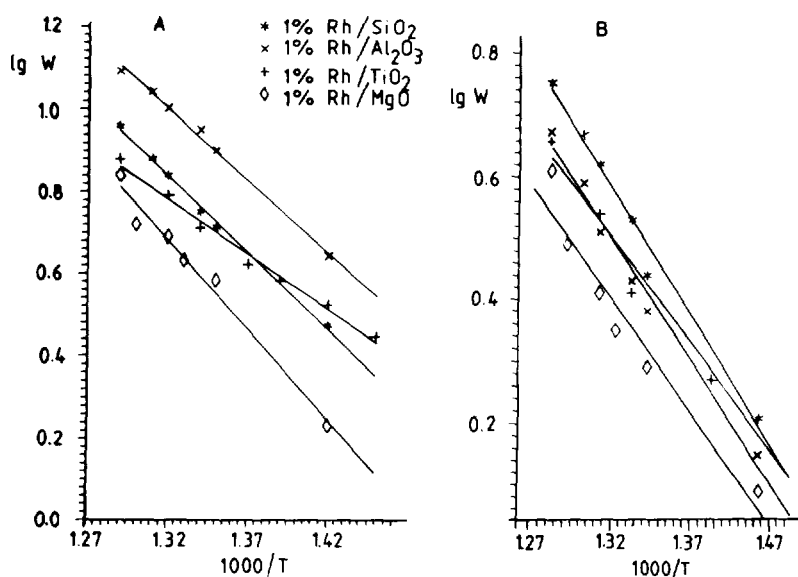
	E_{CO} (kcal/mol)	E_{CH_4} (kcal/mol)	Kinetic order				
			CH ₄		CO ₂		
			CO	H ₂	CO	H ₂	
						a	b
1% Rh/TiO ₂	12.4	15.8	0.29	0.24	0.34	0.2	-0.89
1% Rh/Al ₂ O ₃	16.0	18.2	0.22	0.14	0.43	0.29	-0.6
1% Rh/MgO	20.3	23.2	0.33	0.16	0.38	0.38	-1.0
1% Rh/SiO ₂	17.2	19.1	0.22	0.38	0.23	0.31	0.31

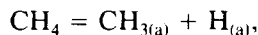
Note. E_{CO} and E_{H_2} , activation energies for CO and H₂ formation. a. The order up to 20% CO₂ content; b. the order above 20% CO₂ content.

temperature at which hydrogen evolution started on Rh film was 323 K at a pressure of 2×10^{-2} Torr of methane (14). From a quantitative study of the CH₄-H₂ 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

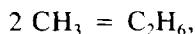
temperature range where the chemisorption of CH₄ took place with H₂ evolution (13, 14). The exchange reaction was also studied on 0.5% Rh/Al₂O₃ catalyst at 593 K, where it occurred quite rapidly (20).

In the present work, the dissociation of CH₄ in a flow system on supported Rh was found above 423 K, when C₂H₆ and H₂ were identified. The primary step is undoubtedly the formation of CH₃,

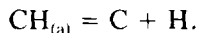
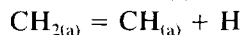
FIG. 8. Arrhenius diagrams for CO (A) and H₂ (B) formation in the CH₄ + CO₂ reaction.



which may dimerize to give C_2H_6 ,



and also decompose further:



Although, the formation of C_2H_6 was observed on all samples in the initial stage of the interaction of CH_4 with Rh catalyst, we did not succeed in identifying any adsorbed CH_3 or CH_x fragments by means of sensitive FTIR measurements. This suggests that the lifetimes of the CH_3 and 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 H_2 obtained compared with that of C_2H_6 indicated that the further dissociation of CH_3 and its complete decomposition occurred in parallel with the dimerization of CH_3 . This process continued for a while even after termination of the formation of C_2H_6 . It is most likely that the surface carbon formed soon blocked the active areas of the metal, and the decomposition of CH_4 ceased.

The dimerization of adsorbed CH_2 and CH species seemed to occur to a very small extent, as there was no indication of the formation of either C_2H_4 or C_2H_2 . Pd/SiO₂ is an exception in this respect as the formation of C_2H_4 was observed besides of C_2H_6 (1).

From the data presented in Fig. 2, it appears clearly that the support exerts a significant influence on the activation of CH_4 and on the further reactions of adsorbed CH_3 species. As regards the decomposition of CH_4 , taking into account the dispersity of the Rh samples, the most effective catalyst was Rh/Al₂O₃. This was followed by Rh/TiO₂, Rh/MgO, and Rh/SiO₂. The amounts of C_2H_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 CO₂ 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 CH_4 and CO₂, 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 CH_4 and the hydrogenation of surface carbon to higher hydrocarbons have recently been proposed as a possible mode of transformation of 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 (α), which can be hydrogenated even below 350–400 K, (ii) a less reactive amorphous layer (β), $T_p = 235$ –495 K, and (iii) the relatively inactive graphitic form (γ), 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 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/SiO₂. The formation of higher hydrocarbons in this reaction up to C₆, has also been observed on Pt/SiO₂ (EUROPRT 1) (3) and on SiO₂ supported Pt metal catalysts (1).

4.2. Dissociation of CO₂

The question of the dissociation of CO₂ 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 CO₂ 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⁻¹ was detected only at and above 573 K. An interesting feature of the interaction of CO₂ 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⁺(CO)₂. Recent EXAFS (25) and IR spectroscopic measurements (26–28) revealed that, because of the CO-induced disruption of Rh clusters, Rh_x-CO species can be transformed into Rh⁺(CO)₂ at 150–423 K. At higher temperatures the reverse process, the reformation of Rh_x-CO from Rh⁺(CO)₂, 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.

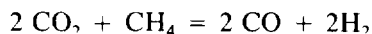
4.3. CH₄ + CO₂ Interaction

When CH₄ was added to the CO₂, 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 CH₄ decomposition promoted the dissociation of CO₂. This is consistent with the previous findings that hydrogen can greatly facilitate this process (15–17).

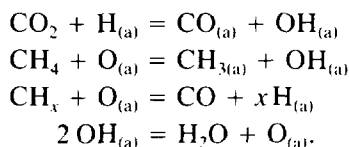
4.4. Catalytic Reaction between CH₄ and CO₂

Although great attention is being paid to the conversion of CO₂ and CH₄ to more valuable compounds, few papers have dealt with the catalytic reaction between CO₂ and CH₄ (2, 4, 29–33), which is commercialized as the Calcor process (29).

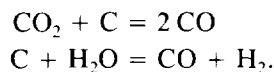
On the Rh samples used in the present study, the CH₄ + CO₂ reaction



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 CO₂ by hydrogen, and perhaps by CH_x fragments, too, the decomposition products of CH₄, and (ii) facilitation of the dissociation of CH₄ by adsorbed O formed in the decomposition of CO₂, which may activate the CH₄ molecule. Accordingly, besides to the steps postulated for the decomposition of the reactants, we may count with the following reactions:



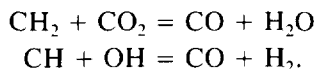
The carbon formed in the dissociation of CH₄ may react either with CO₂, as demonstrated by the results in Fig. 4, or with H₂O,



As the aging of carbon (formed in the dissociation of either CO (8) or CH₄) 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 CH₄ dissociation interacts with CO₂ and H₂O immediately after its production, before the aging process commences.

However, it cannot be excluded that, before their complete dissociation, the CH_x fragments react with CO₂ and H₂O, 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/H₂ 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, CO₂ and water-gas shift reaction. The reported maximum in the H₂ formation rate with increasing CO₂ concentration may be attributed to the latter process.

It is an interesting feature of the high-temperature CH₄ + CO₂ reaction on Rh catalysts that the rates of CH₄ 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 CO₂ (7) and on the NO + CO reaction (34) on the same catalysts prepared in our laboratory. In these reactions, the specific activity of Rh/TiO₂ exceeded that of the less active Rh/MgO and Rh/SiO₂ by almost two orders of magnitude. As the support also exerted a significant influence on the dissociation of CO₂ (Rh/TiO₂ was the most active and Rh/

SiO₂ the least active), it may be concluded that the activation and dissociation of CO₂ do not play an important role in the CH₄ + CO₂ reaction over Rh. In other words, the dissociation of CH₄ and the presence of hydrogen diminish the difference in the effect of the support on the dissociation of CO₂ on Rh.

CONCLUSION

(i) Supported Rh was found to be active in the decomposition of CH₄ to give hydrogen, a smaller amount of ethane, and carbonaceous residues. The activity order was Rh/Al₂O₃, Rh/TiO₂, Rh/SiO₂, 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 CH₄ to CO₂, or vice versa, promotes the dissociation of other compounds. (iv) Supported Rh is active in the high-temperature reaction of CO₂ + CH₄ to give H₂ and CO without carbon deposition.

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