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Decomposition of CH_4 over Supported Pd Catalysts

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The decomposition of methane and its conversion into higher hydrocarbons on supported Pd catalysts have been investigated. The effects of temperature, flow rate, methane content, and support materials have been examined. The dissociation of CH_4 on palladium occurred above 473 K to give hydrogen, a small amount of ethane, and surface carbonaceous species. A significant fraction of hydrogen dissolved into Pd crystallites, which were released only at high temperature, T_p = 600–700 K. The most effective catalyst in the CH_4 decomposition was Pd/TiO_2, whereas a larger amount of ethane was found on Pd/SiO_2. Temperature programmed reactions revealed that different kinds of surface carbon are produced by the decomposition of CH_4. Hydrogenation of these carbonaceous species led to the production of higher hydrocarbons.

1. INTRODUCTION

During the past decade, a great effort has been made to develop an efficient catalyst for the conversion of the cheap raw material methane into C_2 hydrocarbons or oxygenated compounds (1, 2). In the former case, the most effective catalysts are nonreducible oxide mixtures; in the latter case, the transition metal oxides are known to be selective in oxidation processes.

Increasing attention has recently been paid to supported metals, which proved quite active in the decomposition of methane, and additionally they promote the dimerization of methane into ethane (3–9). Our comparative study on silica-supported Pt metals revealed that the most active metal as regards the decomposition of methane was Ru/SiO_2, whereas the highest amount of ethane was produced on Pt/SiO_2 (6). These catalysts were active in the reforming of CH_4 with CO_2 to produce synthesis gas (9–12).

The present paper investigates the decomposition of methane over supported Pd catalysts, with particular emphasis on the formation of ethane and on the reactivity of the surface carbon produced. This work is connected with earlier studies of the thermal stability and reactions of CH_3, CH_2, and CH species on Pd single crystals (13–17) and supported Pd (18). These CH_x fragments were produced on the Pd surface by the thermal- and photoinduced dissociation of different methyl and methylene halides.

2. EXPERIMENTAL

Materials. The catalysts were prepared by impregnating the support with the solution of $PdCl_2$ salts to yield a nominal 5% metal. The following oxides were used: Al_2O_3 (Degussa), TiO_2 (Degussa P25), SiO_2 (Cab-O-Sil), and MgO (DAB 6). 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 673 K *in situ*. After oxidation and reduction the sample was evacuated or flushed with He or N_2 for 15 min. Some characteristic data for the catalysts are collected in Table 1.

The gases used were initially commercial purity. The He (99.996) and the N_2 (99.995) were deoxygenated with an oxytrap. The other impurities were adsorbed a 5A molecular sieve at the temperature of liquid nitrogen.

Methods. The decomposition of CH_4 was investigated in the flow reactor (9): 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 the N_2 stream was switched to N_2 containing 12.5% CH_4. The exit gases were analyzed gas chromatographically (Hewlett–Packard 5890) on a Porapack QS column. The amount of H_2 formed was determined with a thermal conductivity detector. The other products were detected with a flame ionization detector.

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 amount of CO uptake was determined by the pulse method. CO (20.8 μmol) was

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TABLE 1

Some Characteristic Data of Supported Pd Catalysts

	Dispersion (%)	CO_{ads} (μmol/g)	
		Fresh	Used
5% Pd/TiO_2	13.0	42.0	30.9
5% Pd/Al_2O_3	12.8	100.4	53.1
5% Pd/SiO_2	10.7	20.2	16.0
5% Pd/MgO	9.5	23.3	18.9

injected into the fresh or used sample at room temperature until CO consumption was observed.

The temperature-programmed reaction (TPR) and temperature-programmed desorption (TPD) experiments were carried out in the pulse reactor. After the treatment of the sample with CH_4 and the flushing of the surface with N_2 at the temperature of the reaction, the samples were cooled in a N_2 flow to 323 K. For TPR experiments the N_2 flow was then switched to H_2, the sample was heated at 12 K min^{-1}, and the hydrocarbons that had formed were analyzed. In the TPD experiments the carrier gas was N_2 and the desorbed H_2 and CH_4 were analyzed.

The infrared spectroscopic studies were done 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 H_2–O_2 titration at 298 K using the pulse technique (19).

3. RESULTS

3.1. Decomposition of CH_4

The interaction of CH_4 with Pd/SiO_2 was studied first in a flow system by analyzing the products that formed. The evolution of C_2H_6 and H_2 on this Pd sample was registered (Fig. 1). The amount of H_2 was always higher than that of C_2H_6. The initial rate of CH_4 decomposition was high, but gradually decayed to lower values. As indicated by the production of hydrogen and ethane, the decomposition of methane was observed at as low a temperature as 473 K, but C_2H_6 formation was detected only above 473 K. With an increase in the temperature, the rate of product formation increased. The decomposition of CH_4 at the H_2 evolution maximum was 0.05% at 523 K, which increased to 0.64% at 603 K. These values decreased to 0.02% and 0.22%, respectively, after 20 min, and changed only a little afterwards. The C_2H_6/H_2 ratios varied between 0.01 and 0.04. For comparison we mention that the maximum decomposition of CH_4 on Rh/SiO_2 under the same conditions is 1.7% at 523 K, one order of magnitude less than reported (9).

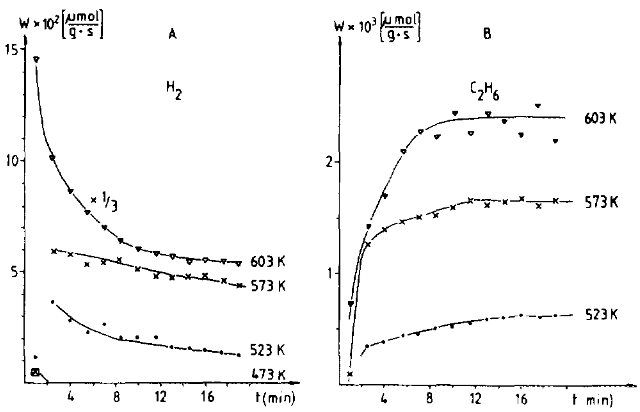

FIG. 1. Effect of temperature on the rates of H_2 (A) and C_2H_6 (B) formation on 5% Pd/SiO_2. Flow rate of N_2 + CH_4 (12.5%), 40 ml/min.

In the next experimental series, the effects of flow rate and CH_4 content were investigated. As demonstrated in Fig. 2, the higher the flow rate, the higher the rate of production of C_2H_6 and H_2. The increase in the C_2H_6 formation rate was higher than that for H_2.

Variation of the CH_4 content in the gas mixture also exerted a significant influence on the rates of production of C_2H_6 and H_2. In pure CH_4, the H_2 formation rate was about two times higher and the C_2H_6 formation rate was more than five times higher than that for the gas mixture containing 12.5% of CH_4 (Fig. 3).

The effects of various supports on the reaction are displayed in Fig. 4. It appears that the rate of decomposition of CH_4 and the product distribution are influenced by the nature of the support. The most effective catalyst for H_2 formation was Pd/TiO_2, followed by Pd/Al_2O_3, Pd/SiO_2, and Pd/MgO. The decomposition of CH_4 on Pd/TiO_2 at 523 K (at the maximum rate) was 0.25%. This value at 773 K, calculated in a similar way, was 4.5%. As regards C_2H_6 formation, the most effective catalyst was Pd/SiO_2. Surprisingly, on Pd/Al_2O_3 and on Pd/TiO_2 only traces of C_2H_6 were observed. On Pd/MgO, ethane formation was

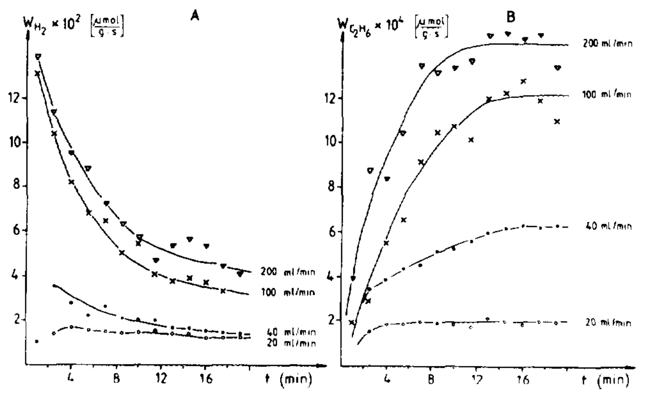

FIG. 2. Effect of flow rate of N_2 + CH_4 (12.5%) on the rates of H_2 (A) and C_2H_6 (B) formation on Pd/SiO_2 at 523 K.

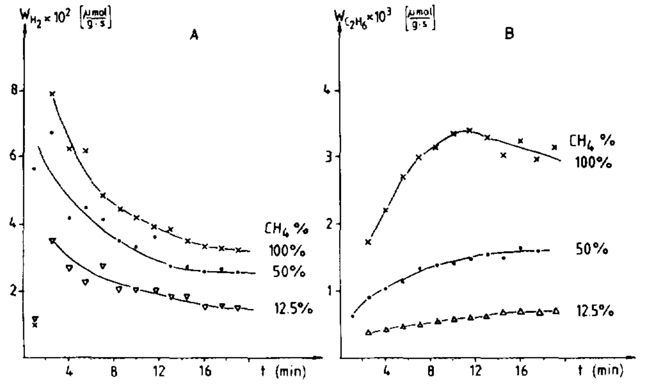

FIG. 3. Effect of CH_4 concentration on the rate of H_2 (A) and C_2H_6 (B) formation on 5% Pd/SO_2 at 523 K. Flow rate of N_2 + CH_4, 40 ml/min.

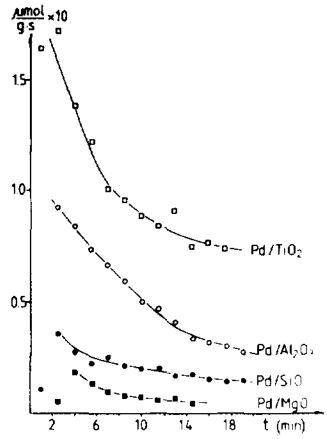

FIG. 4. Effect of supports on the rates of H_2 formation in the decomposition of CH_4 over Pd at 523 K. Flow rate of N_2 + CH_4 (12.5%), 40 ml/min. Amount of catalyst, 0.1 g.

not detected. No reaction of CH_4 occurred on the supports alone. Data for the decomposition of methane are shown in Table 2.

3.2. Examination of Catalysts after Methane Decomposition

TPD measurements carried out after CH_4 decomposition (20 min) at 523 K revealed that a fraction of hydrogen produced in the decomposition remained on the catalyst sample; its evolution occurred in a very broad temperature range, 500–800 K, with T_p values of 600–700 K (Fig. 5A). In addition, a small amount of CH_4 was also released from the catalyst in the temperature ranges 500–700 K and 750–900 K. The amounts of hydrogen and methane thus obtained are shown in Table 2.

In order to assist the interpretation of the hydrogen evolution we performed several control measurements. First, we established that no hydrogen remained in or on the palladium samples after their reduction and flushing with He at 673 K. When the samples have been treated with pure H_2 flow at the temperature of CH_4 decomposition, 523 K, for 20 min, then flushed with He for 10 min, well measurable quantities of H_2 desorbed in subsequent TPD measurements (Fig. 5). The desorption, however, proceeded at lower temperatures, beginning above 400 K and giving smaller amounts of hydrogen compared to those measured after decomposition of CH_4 (Fig. 5B).

The introduction of H_2 into the carrier gas after the reaction produced a significant amount of CH_4 and traces of C_2H_6. These results clearly suggest the deposition of surface carbon on the catalyst during the decomposition of CH_4.

In the following experiments, the reactivity of this surface carbon produced by the decomposition of CH_4 was investigated. It appeared that the temperature of carbon production and the duration of its formation, i.e., the length of time for which the surface was kept at the given temperature, strongly influenced the reactivity of the carbon toward hydrogen and the distribution of its hydrogenation products. Data are collected in Table 3. When the

TABLE 2

Some Characteristic Data of the Decomposition of CH_4 at 523 K on Supported Pd Catalyst

	Initial conversion of CH_4^a (%)	$N_{CH_4}{}^b \times 10^{-3}$ (s^{-1})	$H_2{}^c$ formed (μmol/g)	$H_2{}^d$ dissolved (μmol/g)	$H_2{}^d$ dissolved (μmol/metal)	$CH_4{}^d$ desorbed (μmol/g)	$C_s{}^e$ (μmol/g)	$C_s{}^e$ (μmol/metal)
Pd/TiO_2	0.25	28.0	127.3	24.5	0.4	0.20	9.55	0.15
Pd/Al_2O_3	0.13	15.3	70.2	51.0	0.85	0.13	15.3	0.25
Pd/SiO_2	0.05	7.1	26.9	46	0.91	2.8	34.1	0.68
Pd/MgO	0.02	3.8	8.7	28.5	0.64	2.57	9.22	0.20

[a] Measured at maximum rate.
[b] The turnover frequency of CH_4 decomposition (rates related to the number of surface metal atoms) at the maximum rate.
[c] Determined during the reaction between 1 and 20 min.
[d] Determined by TPD after 20 min of reaction at 523 K.
[e] Determined from the TPR curves of Fig. 6 after the decomposition of CH_4 at 523 K for 20 min. Note that the evolution of CH_4 does not cease even above 900 K.

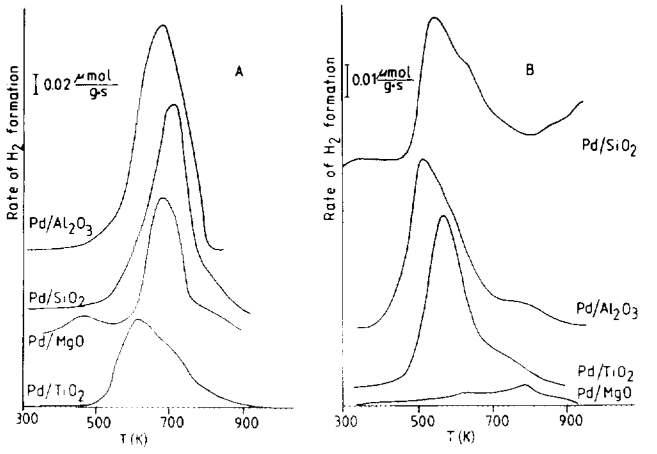

FIG. 5. The amount of H_2 desorbed from Pd samples following the decomposition of CH_4 at 523 K for 20 min (A) and after treatment of fresh catalyst samples with H_2 flow at 523 K for 20 min (B). After the CH_4 decomposition or H_2 adsorption the catalysts were flushed with pure N_2 at 523 K for 5 min; then the samples were cooled to room temperature. Afterwards the samples were heated in a N_2 flow (heating rate was 24 K/min) and the H_2 was analyzed with a thermal conductivity detector.

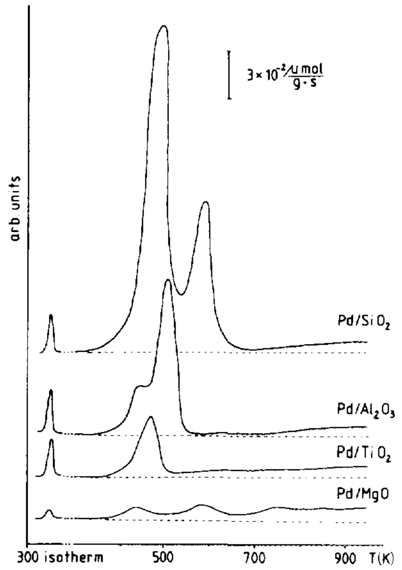

FIG. 6. Temperature-programmed reaction (TPR) of surface carbon with H_2 on supported Pd. Carbon was produced in the decomposition of CH_4 at 523 K for 20 min. The first peak was registered at 323 K under isotherm conditions.

surface carbon was reacted with H_2 pulses at 373 K, the main hydrocarbon product was methane, but ethane and propane were also formed in the first hydrogen pulse. In the second hydrogen pulse, the amount of methane drastically decreased, and ethane and propane were detected only in traces. The extension of the decomposition time of methane from 2 to 20 min did not result in an increased formation of hydrocarbons. Hydrogenation of surface carbon at a higher temperature, 523 K, produced somewhat less methane, and reduced considerably the amount of C_2 and C_3 products (Table 3).

TPR spectra relating to the hydrogenation of surface carbon on different catalyst samples are displayed in Fig. 6. They clearly demonstrate that the support exerts a significant influence on the reaction of the surface carbon with hydrogen. When the surface carbon was produced at 523 K, a very small proportion of it was hydrogenated to CH_4 at slightly above room temperature. This reactive carbon is designated the α form. A larger fraction of the surface carbon (β form) reacted at 400–530 K, with T_p = 450–480 K. In the case of Pd/SiO_2, a high-temperature peak (γ) was also detected, with T_p = 590 K. From the areas of the methane curves, the total amounts of methane evolved were determined: they increased linearly with the reaction time up to 120 min (the highest reaction time used in this experiment). Data for 20 min reaction time are shown in Table 2. The largest amount of methane was found for Pd/SiO_2 and the smallest for Pd/MgO. The value obtained on Pd/SiO_2 was about three times higher when the CH_4 decomposition was followed up to 120 min.

From the data of Table 2 it appears that in the case of

TABLE 3

Formation of Hydrocarbons in the Reaction of 1 H_2 Pulse (41.3 µmol H_2) with Carbon Produced in the Decomposition of CH_4 on Supported Pd (0.3 g) at 523 K

Catalyst	CH_4[a]	C_2H_6[a]	C_3H_8[a]	CH_4[b]	C_2H_6[b] (µmol/g)	C_3H_8[b]	CH_4[c]	C_2H_6[c]	C_3H_8[c]
5% Pd/SiO_2	24.09	—	—	24.78	—	—	24.09	—	—
5% Pd/TiO_2	39.36	0.74	0.0003	37.62	1.212	0.006	33.81	0.0777	—
5% Pd/Al_2O_3	32.49	0.072	—	30.36	0.045	—	29.25	0.006	—
5% Pd/MgO	29.19	0.198	0.0021	28.05	0.39	0.006	27.72	—	—

[a] Decomposition time, 2 min. Temperature of the hydrogenation of carbon, 373 K.
[b] Decomposition time, 20 min. Temperature of the hydrogenation of carbon, 373 K.
[c] Decomposition time; 20 min. Temperature of hydrogenation of carbon, 523 K.

Pd/TiO_2 and Pd/Al_2O_3, only a fraction of carbon was recovered by hydrogenation. This suggests a considerable aging of surface carbon on the catalyst surface.

The uptake of CO by the spent samples was lower than that for the fresh catalysts, but it also indicated that, with the exception of Pd/SiO_2, a significant fraction of Pd is still available for the reaction (Table 1). When the decomposition of methane was performed at 573 K, or the catalyst exposed to methane at 523 K was treated at 573 K, the α peak was missing, and the other methane peaks were shifted to higher temperatures.

The reactivity of surface carbon toward O_2 was also investigated on Pd/SiO_2. Following treatment of the catalyst with CH_4 at 523 K, the reaction with O_2 started at room temperature with T_p = 395 K. A larger fraction reacted above 700 K, with T_p = 980 K.

3.3. Infrared Spectroscopic Measurements

The large amount of hydrogen produced in the interaction of CH_4 with supported Pd indicated the considerable decomposition of CH_4 to CH_x or a surface carbon. In order to identify the surface species formed, we performed detailed infrared spectroscopic mesurements under exactly the same conditions as those under which the decomposition of CH_4 was investigated. We paid particular attention to the frequency region 2800–3000 cm^{-1}, where absorption bands caused by adsorbed CH_3 species are readily detected following the dissociation of CH_3I on Pd/SiO_2 (18). However, we found no spectral indication of the presence of CH_x species during the decomposition of CH_4 at 523–603 K.

4. DISCUSSION

4.1. Dissociation of CH_4

The adsorption and dissociation of CH_4 on Pd films have been investigated previously (20, 21). Although the initial sticking coefficient for methane chemisorption (below the temperature of CH_4 decomposition, i.e., of H_2 formation) was one of the lowest for Pd film (among Cu, Ag, Re, Ni, Mo, W, Ta, and Ti), it was almost the most active in the decomposition of methane at 473 K. The temperature at which hydrogen evolution started on Pd film was 398 K at 2×10^{-2} Torr of methane (21). The decomposition of methane was recently examined on the Pd(679) surface by Wang *et al.* (22). Methane was dissociatively chemisorbed at 1 Torr and surface temperatures $\geq$ 400 K with the formation of surface carbon and hydrogen species. The surface carbon formed fractional monolayers at 400–500 K and a multilayer at 600 K.

In the present work, the dissociation of CH_4 in a flow system on supported Pd was found above 473 K, when C_2H_6 and H_2 were identified. The primary step is undoubtedly the formation of CH_3,

$$CH_4 \rightarrow CH_{3(a)} + H_{(a)},$$

which may dimerize to give C_2H_6,

$$2CH_{3(a)} \rightarrow C_2H_{6(g)},$$

or decompose:

$$CH_{3(a)} \rightarrow CH_{2(a)} + H_{(a)}$$

$$CH_{2(a)} \rightarrow CH_{(a)} + H_{(a)}$$

$$CH_{(a)} \rightarrow C_{(a)} + H_{(a)}$$

$$2H_{(a)} \rightarrow H_{2(g)}.$$

The fact that the rate of the decomposition of CH_4 is enhanced upon an increase in the reactant flow rate, i.e., upon a decrease in the contact time, is probably due to the fact that in this case there is a smaller probability of the reverse reaction:

$$CH_{3(a)} + H_{(g)} = CH_{4(g)}.$$

For the same reason, a high flow rate is also advantageous for the dimerization of adsorbed CH_3 species into C_2H_6, as demonstrated for Pt/SiO_2 (5) and other silica-supported Pt metals (6).

Although the formation of C_2H_6 was observed throughout the decomposition of CH_4 on Pd/SiO_2, we did not succeed in identifying any adsorbed CH_3 or CH_x fragments by means of sensitive IR 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 silica-supported Rh (9).

The larger amount of H_2 obtained compared with that of C_2H_6 indicated that the dissociation of CH_3 occurred in parallel with its dimerization. If we disregard the first, less certain points, the decay in the decomposition of CH_4 (Figs. 1–3) suggests that the surface carbon formed blocks the active areas of the metal. The fact that the formation of C_2H_6 initially increases with the reaction time may mean that a certain deactivation of Pd atoms is required for inhibition of CH_3 decomposition, which assists its recombination. The production of H_2 and C_2H_6, however, does not cease, and both compounds are evolved even after an extended reaction time (120 min). Accordingly, the Pd crystallites are not completely covered by surface carbon. This is supported by the CO chemisorption data, which showed that after CH_4 decomposition for 20 min, a significant fraction of the surface Pd atoms are still available for a reaction (Table 1). In the case of Pd/SiO_2, the amount of surface carbon formed approached the number of surface Pd atoms after 20 min and exceeded it after 120 min of methane decomposition, which suggests that the carbon species produced form clusters, as found for the Pd(679) surface (22), or migrated onto the support.

The dimerization of other adsorbed CH_x fragments seemed to occur to only a very small extent under the present conditions, as C_2H_4 was found merely in traces, and there was no indication of the formation of C_2H_2.

These results are in harmony with those obtained in studies of the reactions of CH_3 and CH_2 species adsorbed on Pd(100) and Pd/SiO_2 surfaces (13–18). It was found that the adsorbed CH_3 species decomposed quickly on Pd, even below 250 K (13–15, 18). Above 300 K, it existed in a detectable concentration only under dynamic conditions, during a continuous flow of CH_3I. The coupling of CH_3 species occurred to only a very limited extent below 250 K. Adsorbed methylene, CH_2, produced by the dissociation of CH_2I_2 also displayed low thermal stability (16, 18). In the low-temperature range, 160–230 K, it was self-hydrogenated into CH_4 and also dimerized to C_2H_4. Above 300 K, it decomposed completely to surface carbon and hydrogen.

The data in Fig. 4 clearly demonstrate that the support exerts a significant influence on the activation of CH_4 and on the further reactions of the adsorbed CH_3 species. As regards the decomposition of CH_4, taking into account the dispersity of the Pd samples, the most effective catalyst was Pd/TiO_2, followed by Pd/Al_2O_3, Pd/SiO_2, and Pd/MgO (Table 2). The amount of C_2H_6 formed in the interaction of CH_4 and the supported Pd catalyst was the highest on Pd/SiO_2. On Pd/TiO_2 and Pd/Al_2O_3, only traces of C_2H_6 were detected. Although it cannot be excluded that the activation of methane on Pd may be affected by the nature of the interaction between the support and the metal (23), which strongly influenced the specific rates of hydrogenation of CO and CO_2 on the same Pd samples (19, 24), we believe that the differences in the present case are mainly associated with the differences in crystal size of the Pd and/or with the ease of carbon migration from the Pd to the support, producing a free Pd surface on the catalyst. The differences in C_2H_6 formation on the Pd samples may be caused by a higher decomposition rate of the produced hydrocarbon on Pd/TiO_2 or Pd/Al_2O_3.

4.2. *Dissolution of Hydrogen*

An interesting feature of the interaction of CH_4 with supported Pd is that a significant fraction of the hydrogen formed in the decomposition of CH_4 remained on or in the Pd and was released only above 500 K. The amount of this hydrogen varied with the support and was in the same order of magnitude of that measured during the decomposition of CH_4 (Table 2). The high temperature release of the hydrogen from the palladium is a strong indication that we are dealing not with adsorbed but rather with dissolved hydrogen in the palladium crystallites (25).

Alternatively, we could assume that CH_x fragments, e.g., CH_2 species, formed in the decomposition of CH_4, dimerize into C_2H_4; a fraction of it is transformed to very stable ethylidyne (CCH_3) species. Accordingly, the high temperature release of hydrogen would be the result of the decomposition of CCH_3. These reaction channels have been established in the decomposition of CH_2I_2 on Pd(100) surface (16). However, even in this case a complete dissociation of ethylidyne occurred below 500 K. In addition, sensitive FTIR spectroscopic measurements (Section 3.3) did not reveal the existence of stable CH_x species on the catalyst surface following CH_4 decomposition.

The fact that we obtained a larger amount of hydrogen compared to the case of hydrogen treatment under same conditions indicates that hydrogen formed in the decomposition of methane on the surface is diffused more easily into the palladium.

The same behavior was observed by Wang *et al.* (22) following the decomposition of methane on a Pd(679) surface at 500–600 K, which was also attributed to the dissolved hydrogen. Interestingly, the peak temperature of hydrogen desorption from Pd(679) (T_p= 730 K) agrees quite well with that measured for Pd/SiO_2 (T_p = 700 K) in the present work. We note here that similar features were observed in the case of the high-temperature decomposition of adsorbed CH_3Cl (26), HCOOH (27), and CH_3OH (28) on K-promoted Pd(100) single-crystal surface under UHV conditions. Further studies on the dissolution of hydrogen formed in surface reactions on supported Pd are desirable.

4.3. *Reactivity of Surface Carbon*

The reactions of the surface carbon were investigated in great detail, as the decomposition of CH_4 and the hydrogenation of surface carbon to higher hydrocarbons have recently been proposed as possible modes of transformation of CH_4 into more valuable compounds (3–8). The main product of the hydrogenation of surface carbon on supported Pd was methane; ethane and propane were also formed. No other hydrocarbons were detected.

The reactivity of the surface carbon toward hydrogen, studied by TPR spectroscopy, exhibited practically the same features as those established for supported Rh (9, 29). 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), with T_p = 235–495 K; and (iii) the relatively inactive graphitic form (γ), which reacts with hydrogen only above 650 K. 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. At and above 573 K, a significant aging was observed, with transformation of the more reactive form into less reactive ones.

CONCLUSION

(i) Methane decomposes on supported Pd above 473 K to yield hydrogen, a small amount of ethane, and surface carbon.

(ii) An increase in the temperature, flow rate, and methane content led to an enhancement of the decomposition.

(iii) The carbon produced very likely forms clusters and leaves a fraction of Pd surface bare as reaction sites. The reactivity of carbon toward hydrogen sensitively depended on the conditions of its formation.

(iv) The hydrogen produced in the methane decomposition exhibited a high tendency to be dissolved into Pd crystallites.

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