JOURNAL OF CATALYSIS **159,** 441–448 (1996)
ARTICLE NO. 0108

Oxygen-Free Conversion of Methane to Higher Alkanes through an Isothermal Two-Step Reaction on Platinum (EUROPT-1)

I. Chemisorption of Methane

Mohamed Belgued, Annie Amariglio,[1] Pierre Paréja, and Henri Amariglio

Laboratoire de Catalyse Hétérogène, Université Henri Poincaré, Nancy I, B.P. 239, 54506 Vandoeuvre Cedex, France

Received April 17, 1995; revised November 1, 1995; accepted November 27, 1995

When submitted to CH_4 at atmospheric pressure, EUROPT-1 (a 6.3 wt% Pt/SiO_2 catalyst) is able to chemisorb CH_4 with parallel evolution of H_2 at $T \geq 150°C$. C_2H_6 is also produced but at a rate approximately 10 times lower, so that H-deficient hydrocarbonaceous fragments build up on the metal surface. Temperature-programed desorption spectra obtained just after chemisorption show that CH_4 can be removed from the surface mainly in two peaks, one at ≈60°C and the second at a temperature varying between 180 and 250°C. Formation of CH_4, accompanied by small amounts of C_2H_6 and traces of C_3H_8, is observed during subsequent temperature-programed surface reaction with H_2 of the adspecies remaining after each TPD interrupted at 300°C. The total amount of CH_4 initially chemisorbed can be easily derived from those experiments and the H/C ratio of the surface species formed during chemisorption can also be estimated. It has been shown that the amount of chemisorbed CH_4 increased and the H/C ratio strongly decreased when the temperature or the duration of exposure was increased. When EUROPT-1 was submitted to (Ar, CH_4) mixtures instead of pure CH_4, the increase of the CH_4 content had an effect similar to that of the increase of either the temperature or the duration of exposure. Moreover the TPD and TPSR spectra are very sensitive to the conditions of the exposure, so that they constitute some fingerprint of the adspecies at the end of the adsorption step.

INTRODUCTION

In recent years direct conversion of CH_4 into more valuable chemicals, especially higher hydrocarbons, has aroused strong interest. By far the most promising and explored route has been oxidative coupling in which the thermodynamic barrier exhibited by the formation of C_2H_6 and C_2H_4 from CH_4 is overcome thanks to the presence of oxygen and the resulting formation of water. Unfortunately O_2 can also cause oxidation of CH_4 to carbon oxides and good selectivity to C_2's cannot be obtained at acceptable yields of conversion.

The potential of metal surfaces as regards CH_4 chemistry seems to have been largely overlooked despite the fact that all the already known catalytic reactions involving CH_4, except for the oxidative coupling, occur on metals: CH_4/D_2 exchange reactions, total oxidation, steam reforming, HCN preparation (Andrussow process), and steam reforming (1). Due to the constraints of thermodynamics, catalytic homologization of CH_4 is not more expectable on metal surfaces than on any other kind of catalyst. The ability of various metals to chemisorb CH_4 at moderate temperatures (2–4) as well as that to decompose CH_4 to C and H_2 at higher temperatures (5, 6) has, however, been known for long. Hence, a two-step process can be imagined where the species formed upon the interaction of CH_4 with the metal surface in the first step in involved in a subsequent suitable step.

Our first report of a possible two-step homologization of CH_4 on Pt (7) illustrated this view, as did the different and almost concomitant contribution by Koerts and van Santen (8). In our preliminary work, as well as in the subsequent one related to the cases of Ru and Co (9), chemisorption of CH_4 (with parallel evolution of H_2) is involved before hydrogenation of the resulting chemisorbed species at a unique and moderate temperature. In the experiments carried out by Koerts and van Santen, methane interacts with Ru or Co at much higher temperatures and formation of bulk or surface carbides is postulated (with complete removal of hydrogen). In order to obtain a mixture of alkanes and not only methane, the following hydrogenation must be effected at a temperature lower than that of the exposure to methane.

Solymosi *et al.* confirmed both procedures by carrying out isothermal as well as dual temperature experiments on a number of supported transition metals (10).

The purpose of the present contribution is to describe the different kinds of experiments which we have carried out on platinum, in a more detailed way than we have done so far, and to discuss the process in the light of these results. In the first part, we will focus on the chemisorption of methane (first step of the homologization process) while the second

---

[1] To whom correspondence should be addressed.

0021-9517/96 $18.00

part is devoted to the hydrogenation of the chemisorbed species (second step).

However, before reporting our results on platinum, it is useful to recall the main experimental data concerning the chemisorption of CH_4 on metals as the reactivity of the derived adspecies.

After the first studies mentioned above (2–6) there has been many reports devoted to the study of CH_4 chemisorption on supported metals, on metal films, or on surfaces of single crystals. Most of the work prior to 1974 was reviewed by Frennet (11). Later on, Pitchai and Klier reviewed most of the contributions up to 1986 (12). We will only focus our attention on the main results which are of interest concerning the possibility of C–C bond formation between C_1 adspecies resulting from chemisorption of CH_4 or related molecules.

First of all, it has been known for a long time that the methane sticking coefficient is very low, ranging from 10^{-10} to 10^{-6} (11). Sizeable coverages, favoring C–C bond formation, cannot therefore be expected under a low pressure of adsorption. In addition, the sticking coefficient appears to be more dependent on the energy of the molecule than on the temperature of the substrate. Ceyer *et al.* explained that the pressure dependence of catalytic reactions involving CH_4, such as the steam reforming, was due to the strong dependence of the sticking coefficient upon the translational and vibrational energy of the molecule (13, 14).

It is a fact that most of the surface science studies focus more on the intimate details of the CH_4 chemisorption than on the fate of the resulting adspecies. A remarkable exception concerns the contributions of Yang *et al.* (15) and of Ceyer (16) who demonstrated the possibility of converting CH_4 into benzene on a Ni (111) surface. CH_4 was first chemisorbed through "collision-induced dissociative chemisorption" and subsequent controlled heatings and readsorptions resulted in the successive formations of CH then C_2H_2 species and finally of C_6H_6 which desorbed at 430 K. C–C bond formation has also recently been reported by Wu and Goodman (17) on Ru(0001) and Ru(11$\bar{2}$0) surfaces after exposure to CH_4 at 5 Torr for 2 min and at temperatures ranging from 130 to 430°C. The only adspecies recognized by HREELS (high-resolution electron energy loss spectroscopy) were methylidyne (CH) and vinylidene $C{=}CH_2$ on Ru(0001) whereas ethylidyne ($C{-}CH_3$) was also evidenced on Ru(11$\bar{2}$0). In twin experiments, hydrogenation of the adspecies, at a temperature lower than that of adsorption, released some ethane and propane (18).

To our knowledge all other contributions on single crystals only showed that dissociative chemisorption leads to CH_x species and different forms of elemental carbon (19–25) which are favored at high temperatures since the stability of CH_x species is questioned beyond 400 K (14, 25, 26).

On supported nickel, formation of CH_x species, with x ranging from 3 to 0, was already postulated by Kubokawa (4), and the possible parallel evolution of H_2 was first reported by Troesch (27). However, only CH_4 was obtained through hydrogenation of the species formed upon previous exposure of supported nickel to CH_4 (11, 28, 29). The first report on C–C bond formation between adspecies arising from CH_4 concerns cobalt (30).

Another way of studying the reactivity of CH_x species on a metal surface consists in bringing them to the surface through dissociative chemisorption of molecules much more reactive than CH_4. Striking results were so obtained by Brady and Pettit on a number of transition metal catalysts with diazomethane that was either pure or mixed with hydrogen (31). Pure diazomethane gave rise to the release of C_2H_4 and N_2 whereas a mixture of hydrocarbons ranging from C_1 to C_{18} was produced on Fischer–Tropsch (F.T.) catalysts in the presence of H_2. This was good evidence that CH_2 can be the building block in F.T. synthesis.

Diazomethane was also used in surface science studies. Berlowitz *et al.* reported the formation of CH_4, C_2H_4, and H_2 during temperature-programed desorption (TPD) following the adsorption of CH_2N_2 at 110 K on Pt(111) (32). Weinberg *et al.* showed, by using electron energy loss spectroscopy (EELS), that the spectra of Ru(001) were the same after the adsorption of either CH_2N_2 or C_2H_4 at 80 K (33).

Ketene (CH_2CO) was used by Ibach *et al.* with Fe(110) (34). After dissociative adsorption at 120 K, CH_2 could remain on the surface up to ca. 250°C. Unstable surface vinylidene species appeared between 130 and 230°C. CH_3 and CH species were also found to coexist with CH_2 and the authors mentioned the existence of "a wealth of phenomena deserving further detailed study."

Methyl halides have also been frequently used as recently reviewed by Chiang *et al.* (35). Dissociation of these molecules into chemisorbed CH_3 and halogen atoms commonly occurs but C–C bond formation was rarely reported (36).

From all these previous studies the possibility that C–C bonds can be formed on metal surfaces sufficiently covered with CH_x species appears not to be questionable.

EXPERIMENTAL

1. Catalyst

Our catalyst was the standard EUROPT-1 catalyst made of 6.3 wt% Pt on silica and has already been well described (37–40). The particle sizes were found to range between 0.9 and 3.5 nm with 75% of the particles smaller than 2 nm in diameter (38). Based upon 105 μmol H_2 chemisorbed dissociatively per gram of catalyst at room temperature (r.t.) and assuming 1 : 1 stoichiometry, the dispersion of Pt is 65% (39), which compares well with the value of

60% detrmined by electron microscopy (38). It was found that 185 to 230 μmol CO g^{-1} and 80 to 100 μmol O_2 g^{-1} chemisorb at r.t. (40).

The catalyst was placed in a continuous flow fixed-bed reactor made of a U-shaped quartz tube (4 mm i.d.) and working at ordinary pressure.

2. Apparatus

The apparatus allowed us to feed the catalyst with H_2, Ar (or He), CH_4, or mixtures of these gases. Except for the reactor made of quartz, the whole apparatus was made of stainless steel tubing with Swagelock fittings, shut-off valves and metallic 4- or 6-port valves. The flows of gases were maintained constant by Brooks flow-controllers. The gases (H_2, Ar, and He, grade U, and CH_4 grade N45, from Air Liquide) were used after purification from O_2, CO, and condensable impurities by standard procedures before feeding the catalyst. We were able to check that no significant O_2 or H_2O traces were present in the gases after purification (<1 ppm) thanks to an O_2-traces analyzer (Mark II Engelhard) and an electrolytic hygrometer (Beckman). Moreover we also checked that the methane contained less than 0.1 ppm of any expectable higher hydrocarbon (in particular C_2H_4 and C_2H_2 were not detected).

After leaving the reactor the gas flow was sent to two gas chromatographs in series. The first one was used for the hydrocarbon analysis and was equipped with a Porapak QS column (1.80 m; i.d., 1.6 mm; 100–180°C) and F.I.D. The second one was used for the H_2 analysis and was equipped with a Carbosphere column (0.6 m; i.d., 2.1 mm; 60°C) and thermal conductivity detection.

3. Procedures

3.1. *Treatment of the Catalyst*

The catalyst was initially reduced in an H_2 flow (50 cm^3/min) during a slow ramp of temperature (1°C/min) up to 450°C, at which temperature it was maintained in the H_2 flow for 15 h. Between two successive experiments the catalyst was submitted to a flow of H_2 at 400°C for 1 h to remove any carbonaceous residue. It was then fed with a flow of Ar (50 cm^3/min) to remove H_2 and finally cooled in Ar (or He) at the temperature desired for the experiment.

3.2. *Determination of the Amount of Chemisorbed CH_4*

After a given exposure of the catalyst to the flow of CH_4, one could expect that the amount of carbonaceous species accumulated on the Pt surface could be determined by reacting them with H_2 and by measuring the quantities of all the alkanes produced, including methane. However, methane originating from the carbonaceous species escaped measurement because it could not be distinguished from that already present in the reactor at the onset of hydrogenation. In order to circumvent this difficulty, the reactor was closed just after the exposure to CH_4 and cooled to r.t. as quickly as possible (ca. 1 min) (we will see in Section 3 of the second article that the flow rate of CH_4 exerts a great influence on the amount of chemisorbed CH_4 and on the H-deficiency of the resulting adspecies, so that a short stay in static CH_4 has no disturbing effect). It could then be cleared of CH_4 by Ar without any desorption. Subsequent feed with H_2 at r.t. caused immediate release of several alkanes, possibly up to C_6, so that the analysis could not be effected in parallel, due to its duration. For this reason we most often preferred to first thermodesorb a part of the chemisorbed species by feeding the catalyst with a flow of Ar and submitting it to a ramp of temperature up to 300°C. A TPD spectrum could so be recorded. The catalyst was then cooled to r.t. once again and thereafter fed with a flow of H_2. No higher alkane formation occurred under these circumstances but in the following TPSR with H_2 (temperature-programed surface reaction) CH_4 was released, accompanied by a much smaller amount of C_2H_6 and by traces of C_3H_8. Apart from giving access to the total amount of CH_4 chemisorbed on the surface, the TPD and TPSR spectra provided us with some kind of fingerprint of the state of the chemisorbed film at the end of the exposure to CH_4.

RESULTS

1. Evolution of H_2 and C_2H_6 during Exposure to CH_4

We have studied the chemisorption of CH_4 at ordinary pressure and at temperatures high enough to make H_2 evolution visible. That turned out to be the case from $T \geq 150°C$. In parallel, evolution of C_2H_6 was also evidenced but at a rate which was roughly ten times lower than that of H_2. The variations of H_2 and C_2H_6 formations versus time on stream are represented in Fig. 1 for different temperatures.

Similar experiments were carried out at 250°C but at lower pressures of CH_4 by using CH_4/Ar mixtures. Formation of C_2H_6 could be evidenced down to 10% CH_4, while H_2 was still evolved at the lowest content of CH_4 (2.5%). At low CH_4 contents, the rate of H_2 formation exhibited a maximum versus time on stream. Table 1 gives the *total* amounts of H_2 and C_2H_6 released from the surface during 1-min exposures of the sample to the flow of the different (Ar, CH_4) mixtures. It can be seen that the amount of C_2H_6 rises more sharply with CH_4 content than does the amount of H_2.

No hydrocarbon other than ethane was formed during the exposure of the sample to methane.

2. Amount of Adsorbed Methane and Its Variation with Operating Factors

In order to determine the amount of adsorbed methane, we proceeded to do a TPD up to 300°C followed by a H_2-TPSR of the remaining adspecies.

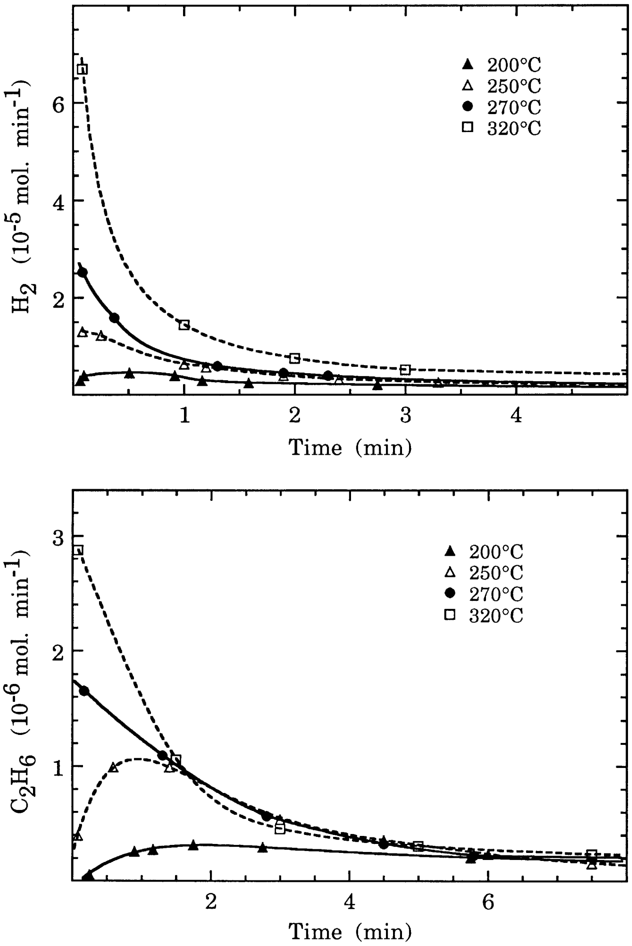

FIG. 1. Molar flow rates of H_2 and of C_2H_6 evolved during exposure of EUROPT-1 to CH_4, as a function of time on stream for different temperatures. Conditions: 100 mg of catalyst exposed to 400 cm^3 min^{-1} of CH_4.

2.1. *TPD Spectra*

After a 1 min exposure of the catalyst to the flow of pure CH_4, the reactor was closed and cooled to r.t. as quickly as possible (1 min or so). Thereafter the reactor was purged with Ar and the TPD was carried out. Only CH_4 was formed during heating. Neither C_2H_6 nor H_2 were visible under any circumstances.

Figure 2 displays the spectra obtained after exposures to CH_4 at four different temperatures. Except for the exposure carried out at 320°C, one can see that CH_4 desorbed in two peaks, well separated and situated at ≈60°C and in the neighborhood of 200°C. The second peak shifted toward the high temperatures when the temperature of exposure was increased.

TABLE 1

Molar Amounts of H_2 and C_2H_6 Evolved during 1-min Exposures to Various (Ar, CH_4) Mixtures at 250°C and Atmospheric Pressure (Flow Rate of (Ar, CH_4), 400 cm^3 min^{-1})

CH_4 content (%)	2.5	10	50	100
H_2 (μmol)	2.41	4.25	9.04	9.95
C_2H_6 (μmol)	0.00	0.02(3)	0.42	0.86

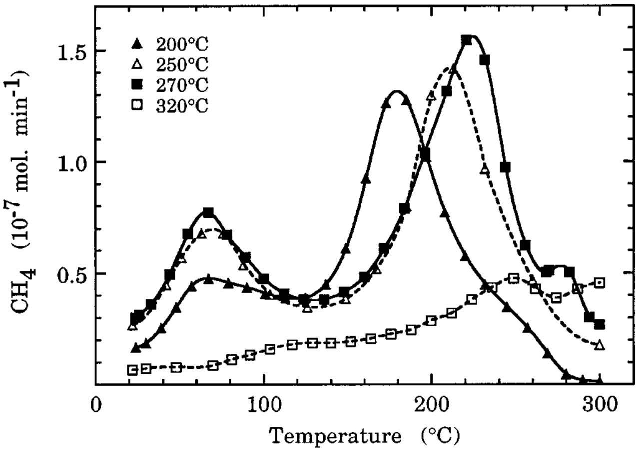

FIG. 2. TPD profiles following exposure of EUROPT-1 to CH_4 at various temperatures. Conditions: Exposure, 100 mg of catalyst exposed to 400 cm^3 min^{-1} of CH_4 for 1 min; flow rate of He, 200 cm^3 min^{-1}; ramp of temperature, 8 K min^{-1}.

2.2. *TPSR Spectra*

The TPDs were always interrupted at 300°C to avoid the risk of forming too much unreactive carbon. After recooling at r.t., the catalyst was then fed with H_2. No CH_4 was formed, so that the temperature could be immediately ramped, which gave rise to the spectra of Figs. 3a–3c.

The main product of TPSR was CH_4, which was accompanied to a lesser extent by C_2H_6 and by traces of C_3H_8. For exposures carried at 250°C, the amounts of CH_4, C_2H_6, and C_3H_8 formed during the TPSR were roughly in the ratios 100 : 10 : 0.3. CH_4 spectra (Fig. 3a) were simpler than their TPD counterparts since each of them mainly consisted of one CH_4 peak situated at ≈340°C. The spectra of C_2H_6 and C_3H_8 (Figs. 3b and 3c) were very similar in shape and exhibited two peaks, the second of them being exactly located at the same temperature as the unique peak of CH_4 (340°C). The first one was obtained at a lower temperature which increased slightly with the exposure temperature.

2.3. *Variation of the Amount of CH_4 Adsorbed versus Temperature*

From the preceding spectra we can easily derive the quantities of each hydrocarbon produced during the different steps of each experiment. All these data are collected in Table 2 and the variation of the molar amount of adsorbed methane versus temperature is represented in Fig. 4.

Those data can be converted into coverages of the Pt surface by CH_x adspecies provided that two assumptions

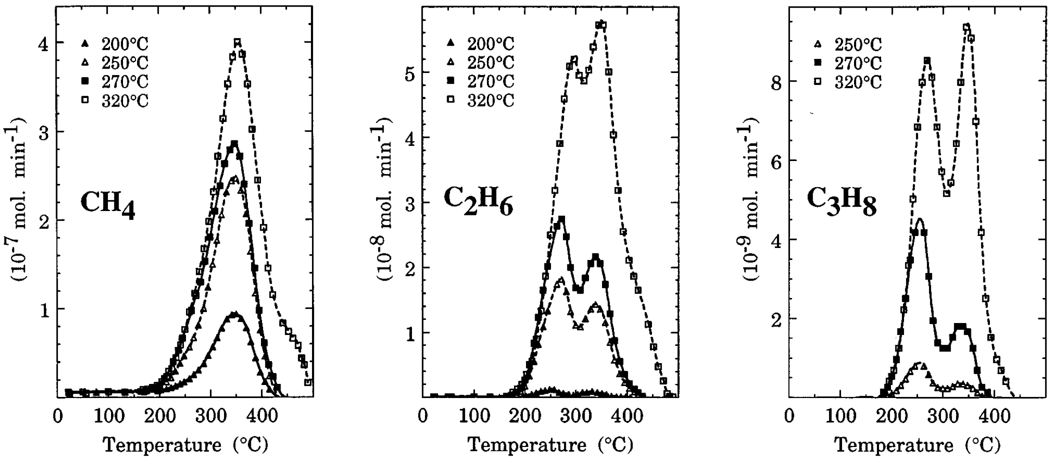

FIG. 3. Profiles of H_2-TPSR of the adspecies remaining on the Pt surface after the TPD corresponding to Fig. 2. Conditions: Flow rate of H_2, 50 cm^3 min^{-1}; ramp of temperature, 6 K min^{-1}.

be accepted: (i) all the C atoms are bonded to Pt atoms and (ii) each of them is bonded to 1 Pt atom only. Based upon the H_2 chemisorption results (see part 1 of the Experimental section), the quantity of surface Pt atoms contained in the sample is 21.0 μmol and the corresponding coverages are represented in Fig. 4.

2.4. Influence of Other Factors

i. The duration of the exposure to CH_4. The influence of the duration of the exposure has been examined at one set of other operating conditions (250°C; pure CH_4 flowing at 400 cm^3/min). The shortest exposure (5 s) is only given as an indication of what follows a brief exposure, due to the poor accuracy concerning the duration of exposure. Every exposure was followed by the same experimental procedure as in the previous cases and the TPD and TPSR profiles (not reported here) allowed us to plot the amount of C_1 units adsorbed on the Pt as well as the corresponding surface coverage with CH_x adspecies as a function of the duration of the corresponding exposure (Fig. 5).

TABLE 2

Molar Amounts of Hydrocarbons Produced during the TPD and the H_2-TPSR after 1-min Exposures to CH_4 at Atmospheric Pressure and Various Temperatures: Corresponding Molar Amounts of Adsorbed Methane (Flow Rate of CH_4, 400 cm^3/min^{-1})

	TPD	TPSR			
Temperature (°C)	CH_4 (μmol)	CH_4 (μmol)	C_2H_6 (μmol)	C_3H_8 (μmol)	$Q_{CH_4\,ads}$ (μmol)
150	0.84	0.95	0.00	0.00	1.79
200	1.75	1.83	0.02	0.00	3.62
250	2.20	4.80	0.37	0.01	7.78
270	2.37	5.66	0.56	0.06	9.33
320	0.85	8.50	1.37	0.19	12.64

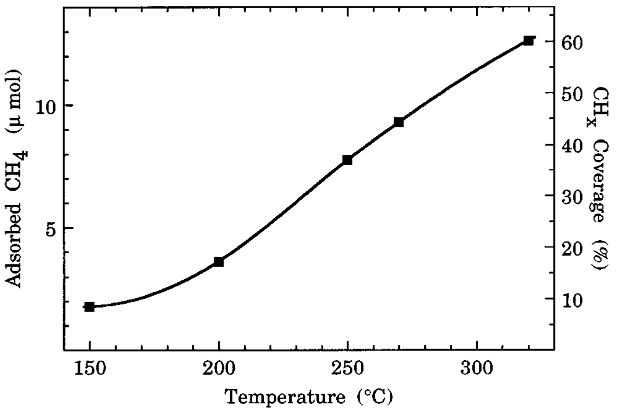

FIG. 4. Variation with temperature of the molar amount of CH_4 adsorbed on 100 mg of EUROPT-1 and of the corresponding surface coverage with CH_x adspecies. Data are deduced from Figs. 2 and 3.

ii. The partial pressure of CH_4 during the exposure. A similar approach was used concerning the role of the partial pressure of CH_4 in the CH_4/Ar mixture to which the catalyst was preliminary exposed. Figure 6 illustrates the increase of the quantity of CH_4 adsorbed (and of the corresponding surface coverage) versus the pressure of CH_4.

DISCUSSION

1. Methane Chemisorption

No just chemisorption of CH_4 was involved during the first step of the reaction sequence since H_2 and C_2H_6 evolution paralleled the sticking of CH_4. The release of H_2 is the result of the association of hydrogen atoms resulting from the dissociative chemisorption of CH_4,

$$CH_4 + 2* \rightarrow CH_{3\,\mathrm{ads}} + H_{\mathrm{ads}}, \qquad [1]$$

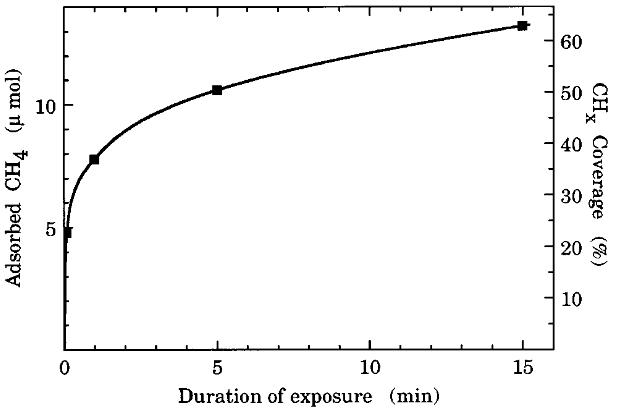

FIG. 5. Variation with the duration of exposure to CH_4 of the molar amount of methane adsorbed on 100 mg of EUROPT-1 at 250°C and of the corresponding surface coverage with CH_x adspecies. Other conditions are the same as for Figs. 2 and 3.

where $*$ stands for a Pt active center. The parallel release of ethane may, in the same way, be seen as the associative desorption of two adsorbed methyls,

$$2CH_{3\,ads} \rightarrow C_2H_6 + 2*, \qquad [2]$$

so that the release of C_2H_6 does not necessarily mean that the C–C bond was initially formed *on* the surface as it would have been the case in the process

$$CH_{3\,ads} + CH_{2\,ads} \rightarrow CH_3 - CH_{2\,ads} + * \qquad [3]$$

followed by

$$CH_3 - CH_{2\,ads} + H_{ads} \rightarrow C_2H_6 + 3\,(\text{or } 2)\,*. \qquad [4]$$

Besides, we must notice that association between CH_3 and CH_2 species chemisorbed on metal surfaces has been considered as not probable on theoretical bases (41, 42).

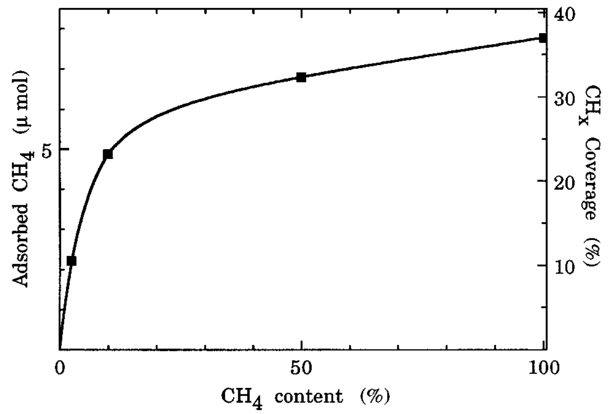

FIG. 6. Variation with the CH_4 content of the amount of methane adsorbed from (Ar–CH_4) mixtures on 100 mg of EUROPT-1 at 250°C and of the corresponding surface coverage with CH_x adspecies. Other conditions are the same as for Figs. 2 and 3.

However thermodynamically unfavored, the dehydrogenative coupling of CH_4 might be assumed to be catalyzed by Pt. However, as the rate of evolution of C_2H_6 was roughly ten times lower than that of H_2, other processes than those involved in the coupling of CH_4 must have necessarily taken place, resulting in the progressive accumulation of H-deficient CH_x species on the surface during the exposure to CH_4, which led the adsorption and desorption processes to extinction.

Desorption of CH_4 during TPDs was direct evidence that the hydrogen contained in the methane having reacted with the surface had not been completely removed. We may reasonably assume that part of the remaining hydrogen was present in CH_x or C_nH_y adsorbed species, whereas the rest of it was simply adsorbed on Pt atoms.

We can evaluate approximate averages of the H/C ratio of the chemisorbed species, which we call x, in two ways.

First, we can remark that the total molar amount of CH_4 having reacted with the Pt surface, $Q_{CH_4\,tot}$, is

$$Q_{CH_4\,tot} = Q_{CH_4\,ads} + 2Q_{C_2H_6\,des},$$

where $Q_{CH_4\,ads}$ is the molar quantity of C_1 units adsorbed at the end of the first step and $Q_{C_2H_6\,des}$ is the molar amount of C_2H_6 released during the same period of time. The corresponding total amount of H_2 involved is

$$Q_{H_2\,tot} = 2Q_{CH_4\,tot}.$$

If Q_{HS} means the molar amount of superficial hydrogen, whether bonded to Pt or to C, and if $Q_{H_2\,des}$ is the total amount of H_2 desorbed during the first step, we can write

$$Q_{HS} = 2Q_{H_2\,tot} - 2Q_{H_2\,des} - 6Q_{C_2H_6\,des}.$$

Q_{HS} is therefore accessible to measurement since $Q_{CH_4\,tot}$ can be derived from $Q_{C_2H_6\,des}$ and from the results of TPD and TPSR spectra. Now if we neglect the hydrogen chemisorbed on the metallic atoms and therefore if we assume that all the hydrogen left on the surface is bonded to surface carbon, we obtain a first limiting value of the H/C ratio, x_1, such as

$$x \le x_1 = \frac{Q_{HS}}{Q_{CH_4\,ads}} = 4 + 2\frac{Q_{C_2H_6\,des} - Q_{H_2\,des}}{Q_{CH_4\,ads}}.$$

In another way, we may roughly consider that if the rate of methane desorption is so low at the end of the TPD (300°C) it is because there only remains a negligible amount of hydrogen bonded to the metal. This assumption concerning the situation prevailing on the surface at the end of the TPD has more chance to hold than just at the end of exposure. If so, the total H-content of the surface at the end of its exposure to CH_4 is 4 $Q_{CH_4\,TPD}$ if $Q_{CH_4\,TPD}$ represents the total amount of CH_4 removed during the TPD. We can thus

TABLE 3

Evaluation of x_1 and x_2 (See Text) at Different Temperatures

T (°C)	$Q_{H_2 \text{ des}}$ (μmol)	$Q_{C_2H_6 \text{ des}}$ (μmol)	$Q_{CH_4 \text{ TPD}}$ (μmol)	$Q_{CH_4 \text{ ads}}$ (μmol)	x_1	x_2
150	0.57	0.00	0.84	1.79	3.4	1.9
200	4.00	0.15	1.75	3.62	1.9	1.9
250	9.90	0.86	2.20	7.78	1.7	1.1
270	15.5	1.51	2.37	9.33	1.0	1.0

Note. Conditions: 1 min exposure to CH_4; 400 cm^3 min^{-1}; 1 atm.

reach another limiting value of the H/C ratio, x_2 such as

$$x \leq x_2 = 4\frac{Q_{CH_4 \text{ TPD}}}{Q_{CH_4 \text{ ads}}}.$$

The values of x_1 and x_2 related to two sets of experiments are reported in Tables 3 and 4. One can notice that x_1 and x_2 differ most when they relate to exposures which can be expected to produce little dehydrogenation of the adspecies (low temperature or short duration) and can accordingly result in sizeable coverages of the surface with H nonbonded to carbon. This remark is moreover supported by the fact that x_1 then exceed 3. The x_2 values, more reliable than x_1 ones, clearly show that the adspecies present on the Pt at the end of most of our exposures to CH_4 exhibited strong H-deficiency. Values of x lower than 2 make highly probable the formation of adsorbed methylene and methyne, between which C–C bonding can reasonably be expected. No energy barrier was theoretically found for the reaction of two methylenes and they were accordingly considered to be able to couple spontaneously (36).

A question which may now naturally be raised concerns the reason why no unsatured hydrocarbons, in addition to ethane, were formed during exposure to methane. We suggest that this is because their binding energy to the metal is so high that heating over the temperature of experiment should be necessary but cracking would then be expected to interfere with desorption. Displacement by another species is easier and we have reported the results of CO-induced desorption of at least part of the species present on Pt after its exposure to methane (43). Numerous alkanes and olefins ranging up to C_8 or C_9 could so be obtained.

TABLE 4

Evaluation of x_1 and x_2 (See Text) for Exposures of Different Duration

Duration	$Q_{H_2 \text{ des}}$ (μmol)	$Q_{C_2H_6 \text{ des}}$ (μmol)	$Q_{CH_4 \text{ TPD}}$ (μmol)	$Q_{CH_4 \text{ ads}}$ (μmol)	x_1	x_2
5 s	1.10	0.00	1.30	4.80	3.5	1.1
1 min	9.90	0.86	2.20	7.78	1.7	1.1
5 min	22.9	3.30	1.50	10.3	0.2	0.6
15 min	31.5	4.50	0.50	13.2	0.0	0.2

Note. Conditions: exposures carried out at 250°C; 400 cm^3 min^{-1}; 1 atm.

2. TPD and TPSR

The main object of obtaining the TPD and TPSR profiles was to determine the amount of CH_4 chemisorbed during each exposure. The rather intricate shape of these profiles and their definite sensitiveness to the exposure conditions show that they can constitute some fingerprint of the global chemical state of the adspecies at the end of the adsorption step. Some features of the TPD profiles are easily understood. For example the relatively small amount of CH_4 thermodesorbed after adsorption at 320°C (Fig. 2), notwithstanding the fact that, under our conditions, the surface attained the largest coverage at that temperature, clearly illustrates the corresponding great H-deficiency of the adspecies.

Most of the methane involved in TPD appeared in two main peaks occurring at greatly different temperatures. One of them, at about 65°C, must reasonably be ascribed to the associative desorption of little dehydrogenated C_1 adspecies and hydrogen. The second one is exhibited at temperatures higher by 100°C at least and may thus be understood as resulting primarily from breaking of C_{2+} adspecies. As its position varies by as much as 60°C, depending upon the adsorption temperature, it is highly probable that various C_{2+} adspecies contribute to this second TPD peak of CH_4 in proportions which greatly depend upon the conditions of the preliminary adsorption.

Once the catalyst has been cooled to r.t. after the TPD, feeding it with H_2 does not entail any CH_4 production. In fact, CH_4 does not reappear before 200°C during the progress of the subsequent TPSR.

The TPSR profiles look simpler than the TPD ones in that they mainly consist of a unique peak of methane. Ethane and propane are also produced but to a less extent and they give rise to two peaks (see Fig. 3). Contrasting with the high-temperature TPD peaks, the first peaks exhibited in the TPSR profiles related to C_2H_6 and C_3H_8 appear somewhat sensitive to the exposure conditions whereas the second ones are almost totally insensitive to them, insofar as only the position of their maxima is considered. Furthermore, there is a very good correspondence between the methane peak and the second peaks of ethane and propane.

Those observations first demonstrate that no more reactive C_1 adspecies remain on the surface after TPD. In the second place, we suggest that, due to the dehydrogenation (loss of CH_4) and to the molecular rearrangements having taken place during the TPD, only some strongly H-deficient carbonaceous fragments are still present on the Pt surface. Their total amount, more than their nature, must depend upon the conditions of the initial exposure to CH_4. From their reaction with H_2, mainly CH_4 is produced, accompanied by small quantities of C_2 and C_3 at rather well-defined temperatures.

3. Yield of the Reaction of CH_4 with the Platinum Surface

In each of the experiments described in the present report, the chemisorbed methane represented but a very small fraction of the total methane sent to the catalyst. For example, Table 2 shows that the quantity of chemisorbed methane ranged from 1.79 to 12.6 μmol whereas 400 cm^3 of CH_4 at ambient conditions was used, i.e., a CH_4 quantity close to 16 mmol. The yield of adsorption with respect to CH_4 ranged therefore roughly from 0.16 to 0.79‰. However, we must note that the Pt is by far the limiting reactant since the sample used was not able to chemisorb more than 21 μmol of CH_4 at full coverage (upon the assumption that C/Pt_S be equal to 1), which would correspond to a limiting adsorption equal to 1.3‰ of the incoming CH_4. The corresponding fraction of the surface Pt atoms which was utilized ranged from 8.5 to 60%.

What makes the conversion of CH_4 so small is the fact that an elevated flow rate of CH_4 was used instead of contacting the sample with static methane in a closed reactor of limited volume. However, in the latter case no sufficient dehydrogenation of the adspecies would have resulted and consequently no C–C bonding would have taken place, as is shown in the following article. The simplest way of removing H_2 was to use flowing CH_4 itself for carrying the desorbed H_2 out of the reactor. We did so but at the cost of wasting a large quantity of CH_4. Other means can be imagined to obtain C–C bonding between the adspecies while saving CH_4 as discussed in the next article.

CONCLUSION

Despite its low reactivity, methane can react with platinum at moderate temperatures. The chemisorption of methane is accompanied above 150°C by the release of H_2 and of lower quantities of C_2H_6, so that carbonaceous adspecies can build up. H-deficiency of these adspecies increases with the temperature and with the prolongation of the exposure to CH_4. Therefore C–C bond formation can be expected between neighbor H-deficient CH_x species. In the subsequent paper we will report on the results of the hydrogenation of these adspecies.

REFERENCES

1. Satterfield, C. N., "Heterogeneous Catalysis in Industrial Practice," 2nd ed, p. 320. McGraw–Hill, New York, 1991.
2. Morikawa, K., Benedict, W. S., and Taylor, H. S., *J. Amer. Chem. Soc.* **57**, 592 (1935).
3. Morikawa, K., Benedict, W. S., and Taylor, H. S., *J. Amer. Chem. Soc.* **58**, 1445 (1936).
4. Kubokawa, M., *Rev. Phys. Chem. Jpn..* **12**, 157 (1938).
5. Scheffer, F. E. C., Dokkum, T., and Al, J., *Rec. Trav. Chim.* **45**, 803 (1926).
6. Kubokawa, M., *Rev. Phys. Chem. Jpn.* **11**, 82 and 96 (1937).
7. Belgued, M., Paréja, P., Amariglio, A., and Amariglio, H., *Nature* **352**, 789 (1991).
8. Koerts, T., and van Santen, R. A., *J. Chem. Soc. Chem. Commun.* 1281 (1991).
9. Belgued, M., Amariglio, H., Paréja, P., Amariglio, A., and Saint-Just, J., *Catal. Today* **13**, 437 (1992).
10. Solymosi, F., Erdöhelyi, A., and Cserényi, J., *Catal. Lett.* **16**, 399 (1992).
11. Frennet, A., *Catal. Rev. Sci. Eng.* **10**, 37 (1974).
12. Pitchai, R., and Klier, K., *Catal. Rev. Sci. Eng.* **28**, 13 (1986).
13. Lee, M. B., Yang, Q. Y., Tang, S. L., and Ceyer, S. T., *J. Chem. Phys.* **85**, 1693 (1986).
14. Lee, M. B., Yang, Q. Y., and Ceyer, S. T., *J. Chem. Phys.* **87**, 2724 (1987).
15. Yang, Q. Y., Johnson, A. D., Maynard, K. J., and Ceyer, S. T., *J. Amer. Chem. Soc.* **111**, 8748 (1989).
16. Ceyer, S. T., *Langmuir* **6**, 82 (1990).
17. Wu, M. C., and Goodman, D. W., *J. Amer. Chem. Soc.* **116**, 1364 (1994).
18. Lenz-Solomun, P., Wu, M. C., and Goodman, D. W., *Catal. Lett.* **25**, 75 (1994).
19. Beebe, T. P., Jr., Goodman, D. W., Kay, B. D., and Yates, J. T., Jr., *J. Chem. Phys.* **87**, 2305 (1987).
20. Luntz, A. C., and Bethune, D. S., *J. Chem. Phys.* **90**, 1274 (1989).
21. Luntz, A. C., and Harris, J., *Surf. Sci.* **258**, 397 (1991).
22. Harris, J., Simons, J., Luntz, A. C., Mullins, C. B., and Rettner, C. T., *Phys. Rev. Lett.* **67**, 652 (1991).
23. Hanley, L., Xu, Z., and Yates, Jr., *Surf. Sci.* **248**, L265 (1991).
24. Chorkendorff, I., Alstrup, I., and Ullmann, S., *Surf. Sci.* **227**, 291 (1990).
25. Wang, Y. N., Herman, R. G., and Klier, K., *Surf. Sci.* **279**, 33 (1992).
26. Stuve, E. W., Madix, R. J., and Brundle, C. R., *Surf. Sci.* **152/153**, 532 (1985).
27. Troesch, A., *J. Chim. Phys. Physicochem. Biol.* **47**, 274 (1950).
28. Kuijpers, E. G. M., Breedijk, A. K., van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **72**, 210 (1981).
29. Kuijpers, E. G. M., Breedijk, A. K., van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **81**, 429 (1983).
30. Tanaka, K. I., Yaegashi, I., and Aomura, K., *J. Chem. Soc. Chem. Commun.* 938 (1982).
31. Brady, R. C., and Pettit, R., *J. Amer. Chem. Soc.* **102**, 6181 (1980).
32. Berlowitz, P., Yang, B. L., Butt, J. B., and Kung, H. H., *Surf. Sci.* **159**, 540 (1985).
33. George, P. M., Avery, N. R., Weinberg, W. N., and Tebbe, F. N., *J. Amer. Chem. Soc.* **105**, 1393 (1983).
34. Mc Breen, P. H., Erley, W., and Ibach, H., *Surf. Sci.* **148**, 292 (1984).
35. Chiang, C-M., Wentzlaff, T. H., and Bent, B. E., *J. Phys. Chem.* **96**, 1836 (1992).
36. Ali, A. K. M., Saleh, J. M., and Hikmat, N. A., *J. Chem. Soc., Faraday Trans. 1* **83**, 2391 (1987).
37. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18**, 221 (1985).
38. Geus, J. W., and Wells, P. B., *Appl. Catal.* **18**, 231 (1985).
39. Frennet, A., and Wells, P. B., *Appl. Catal.* **18**, 243 (1985).
40. Wells, P. B., *Appl. Catal.* **18**, 259 (1985).
41. Zheng, C., Apeloig, Y., and Hoffmann, R., *J. Amer. Chem. Soc.* **110**, 749 (1988).
42. De Koster, A., and van Santen, R. A., *J. Catal.* **127**, 141 (1991).
43. Amariglio, H., Belgued, M., Paréja, P., and Amariglio, A., *Catal. Lett.* **31**(1), 19 (1995).