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Oxygen-free Conversion of Methane to Higher Hydrocarbons through a Dual-Temperature Two-Step Reaction Sequence on Platinum and Ruthenium

2. Removal of Products at a Fixed Temperature

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In order to study the effect of the temperature (T_{CH_4}) at which the catalysts were exposed to CH_4 upon the C_{2+} products of the further hydrogenation, the latter process was conducted at a fixed temperature (T_{H_2}) while different values were ascribed to T_{CH_4} in a set of successive experiments. T_{CH_4} did not exceed 320°C. Different sets were effected, corresponding to different values of T_{H_2} (from room temperature to 200°C). If $T_{H_2} \leq 120$°C hydrogenolysis was negligible, so that the variations of the production were only due to the changes affecting the adlayer. On both catalysts and at every value of T_{H_2}, the production displayed a maximum versus T_{CH_4}. On Pt, the selectivity to ethane and propane at a given T_{H_2} monotonically decreased when T_{CH_4} increased while that corresponding to the heavier products (C_6–C_8) increased. In contrast, on Ru, the selectivities to ethane and propane exhibited a minimum versus T_{CH_4} while those to heptanes and octanes exhibited a maximum. The results are interpreted by assuming that, during the chemisorption of CH_4, several families of hydrocarbon precursors of different weights and shapes are formed on the metal surfaces. It must be assumed that, on Pt, the average weight of the precursors was an increasing function of T_{CH_4}, whereas on Ru it displayed an optimum in the upper part of the explored range of T_{CH_4}. No appreciable amount of unreactive carbon was formed under the conditions of the described experiments. © 1998 Academic Press

INTRODUCTION

In our preceding contribution (1) we have reported a part of the results obtained with silica-supported Pt and Ru catalysts by feeding them successively with CH_4 and H_2. We have mainly been interested in dual-temperature experiments and especially in various series of experiments comprising a given exposure to CH_4 at a fixed temperature, T_{CH_4}, as a first step, followed by hydrogenation/desorption of the resulting adspecies at a lower temperature, T_{H_2}, as a second step. The interest of this approach lies in the fact that only the second step was responsible for the variations of the amount of the homologated CH_4 and of the product distribution since the adlayer resulting from the first step remained the same in a given series of experiments.

We are now reporting on the results of complementary experiments whose second steps (hydrogenations) have been carried out at a fixed T_{H_2} in a given series, following exposures to CH_4 conducted at various T_{CH_4} in the successive experiments of the series. So doing, the changes affecting the results could originate but in the modifications undergone by the adlayer, due to the choice of T_{CH_4}. Moreover, by adequately choosing T_{H_2}, the hydrogenolysis of the products could be rendered negligible.

The composition of the adlayer resulting from exposure of a metal surface to molecules able to give rise to chemisorbed carbonaceous species is expected to depend upon the nature of the metal, that of the molecules, and the conditions of the exposure. In catalytic studies it has become a common practice to submit the adspecies to TPSRs (temperature programmed surface reactions) in order to get a kind of fingerprint of the possible various species present on the surface. In the case of surfaces exposed to hydrocarbons, different forms of C are expected from decomposition of the species. It is frequently in terms such as C_α, C_β, and C_γ that the composition of the adlayer is described, due to the frequent presence of three main methane peaks in the H_2-TPSR. To our knowledge, McCarty and Wise were the first to adopt this terminology in a study devoted to the case of an alumina-supported Ni catalyst (2). However, only two peaks resulted from an exposure to CO. The first one, which they called C_α, exhibited its maximum at $T_p \approx 200$°C and the second one, named C_β, occurred at $T_p \approx 400$°C, but it was very broad and extended itself above 600°C. A third peak, named C_γ (at $T_p \approx 280$°C and partly overlapping C_α) was formed upon exposure of the same catalyst to C_2H_4. Another peak, $C_{\alpha'}$, could appear as a shoulder on the ascending branch of C_α and originated in a very reactive form

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of carbon deposit able to react from ≈50°C or even room temperature (r.t.). They proposed to identify C_α as isolated carbon atoms, possibly C_2, bonded to Ni atoms, $C_{\alpha'}$ as a similar species, but bonded to surface defects, C_β as a polymerized form of carbon like that already described as consisting of graphitic domains, about 15 Å in size, on Ni(110) (3–5) and Ni(001) (6). C_γ, formed only from ethylene in their study, was identified as superficial Ni_3C.

The carbonaceous species present on the surface of silica-supported Ru catalysts under the conditions of Fischer–Tropsch synthesis have been extensively studied by Bell's group. Four forms of nonoxygenated adspecies were identified with isotopic tracers and ^{13}C NMR spectroscopy (7–11). One form, C_α, also called carbidic carbon, was considered to be easily convertible to CH_4 and higher alkanes. Another form, C_β, was viewed as constituted of two kinds of alkyl groups, $C_{\beta1}$ and $C_{\beta2}$, differing by their mobilities on the surface and, finally, the unreactive graphitic carbon was called C_γ. In a further study devoted to the case of a TiO_2-supported Ru catalyst, the C_β species was differentiated into $C_{\beta'}$, intermediate to C_{2+} alkanes, and $C_{\beta''}$, supposed to consist of longer alkyl chains residing on the support (12).

In their contribution to the study of the possible conversion of CH_4 to higher alkanes by a two-step reaction sequence, Koerts *et al.* also recognized three classes of carbonaceous adspecies to which similar names were ascribed (13). These authors considered that C_α is the adspecies whose hydrogenation leads to the formation of C_{2+} alkanes and, in agreement with the previous NMR studies by Bell *et al.*, they also considered that C_α has only metal atoms in its first coordination shell.

In the case of a silica-supported Ru catalyst, exposed to a single or successive pulses of CH_4, Carstens and Bell observed the possible formation of C_α, hydrogenatable at less than 100°C, C_β, hydrogenatable between about 120 and 350°C and C_γ, the least reactive form of carbon ($T_p > 400°C$), interpreted as graphitic carbon (14). The proportions of these different adspecies were obviously dependent upon the conditions of their formation. A more detailed examination allowed the authors to subcategorize C_α into $C_{\alpha1}$, which could react at r.t. (or less) and $C_{\alpha2}$, reacting between r.t. and 100°C. C_β could also be subcategorized into three adspecies, i.e. $C_{\beta1}$ and $C_{\beta3}$, only formed on carburized Ru, and $C_{\beta2}$, formed on carburized or noncarburized Ru. Due to aging in stagnant He, $C_{\beta1}$ could give rise to C_γ. Aging also caused the growth of $C_{\alpha2}$ and $C_{\beta1}$ at the expense of $C_{\beta2}$ while C_γ seemed to be irreversibly formed. Ethane was the main homologated product and was mostly released from carburized ruthenium on which C_α and C_γ were more favored than C_β.

A great deal of surface science studies, using the electron spectroscopies commonly associated with them, has been accomplished to identify the various carbonaceous adspecies able to be formed on metal surfaces mainly, but not uniquely, from exposures to ($CO + H_2$). The corresponding contributions published before 1981 were reviewed by Biloen and Sachtler (15). At least two of their results are directly related to the subject of the present work. One is that two main kinds of deposits can be distinguished: a little reactive graphitic carbon and a much more reactive adspecies named carbidic carbon. The second is that the carbidic carbon is heterogeneous in nature since it can consist of adsorbed carbon atoms, CH_x adspecies, and polymeric units involving C–C bonds. Graphitic carbon can therefore be unambiguously classed as C_γ, whereas carbidic carbon may encompass C_α as well as C_β if C_α is considered to be deprived of C–C bondings. Among the more recent reports we attach a particular significance to those revealing differences between the results of exposures to either CO (possibly added to H_2) or hydrocarbonaceous molecules (16, 17) and also to those which show the existence of C–C bondings between adspecies stemming from exposures to methane prior to the supply of hydrogen. The latter case is illustrated in the contribution by Wu and Goodman (18) concerning the adsorption of CH_4 on Ru(0001) and Ru(11$\bar{2}$0). From detailed examination of various spectroscopic results concerning carbidic layers formed on Ni(100) and Ni(111) during exposures to CO or to C_2H_4, Hutson *et al.* concluded that significant amounts of C–C bonds were present on the surface, thus revealing the existence of adspecies containing 2, 3, or more carbon atoms (19).

We will now report on our results and we will try to show how they can give some insight into the composition of the adlayers originating in CH_4 chemisorption on Pt and Ru.

PROCEDURES AND CATALYSTS

The apparatus, the methods and the catalysts samples are exactly those which have been described in the preceding article (1).

RESULTS

Increasing coverages of the metal surface were expected from exposures to CH_4 conducted at increasing temperatures in successive separate experiments, other experimental conditions being fixed. We will essentially consider here the results of hydrogenations at fixed T_{H_2} (total C_{2+} productions and product distributions successively) and report their variations with T_{CH_4}. We will pursue by reporting the results of H_2-TPSR's following exposures to CH_4 conducted at various temperatures.

1. Experiments Corresponding to a Fixed T_{H_2}

1.1. C_{2+} Productions

Figures 1 and 2, respectively, represent the results obtained at $T_{H_2} = 100°C$ on Pt and $T_{H_2} = 120°C$ on Ru. They give

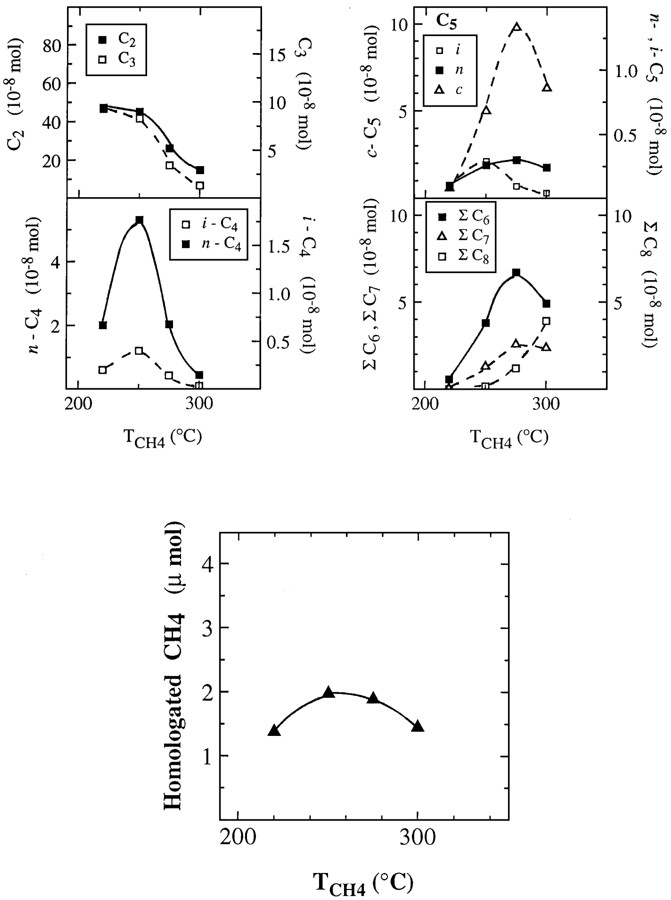

FIG. 1. Variations with T_{CH_4} of the molar amounts of the total homologated methane and of the various C_{2+} alkanes resulting from the exposure of 100 mg of **EUROPT-1** to methane at T_{CH_4} (step 1) and subsequent hydrogenation at a fixed T_{H_2} (100°C) (step 2). Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 1 min, T_{CH_4}); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, 100°C).

the detailed productions of the various C_{2+} hydrocarbons, as well as the total amounts of homologated CH_4. Except for one particular value of T_{CH_4} for each metal (300 and 240°C for Pt and Ru, respectively) the detailed productions reported here have not been given in our previous contribution (1). The total amounts of homologated CH_4 can be found among the data of our previous contribution but it is natural and useful to plot them here versus T_{CH_4} whose effect is specifically studied in the present work. For both metals, most remarkably, the total C_{2+} production exhibited a maximum versus T_{CH_4} which was more pronounced, however, in the case of Ru. On this latter metal, corresponding maxima were also present in the productions of each C_{2+} product, but on Pt such was not the case for ethane and propane which monotonically decreased and for the octanes which increased through the whole range of temperatures. The T_{CH_4} values maximizing each alkane production tended to increase with the weight of the alkane.

Results quite similar to the preceding ones were obtained with each metal at other settings of T_{H_2}. The corresponding total C_{2+} productions versus T_{CH_4} are collected in Figs. 3 and 4. As concerns Pt (Fig. 3), the curves showed a maximum at approximately the same value of T_{CH_4} (260–265°C), irrespective of the value of T_{H_2}. Octanes were formed even at r.t. if T_{CH_4} was higher than 275°C, whereas a maximum appeared for ethane and propane if T_{H_2} was fixed at 200°C. On Ru (Fig. 4), at T_{H_2} equal to 22 or 80°C, only the decreasing branch of the curve representing the variations of the amount of the total homologated methane versus T_{CH_4} was obtained, which reflected the same situation than for the detailed curves corresponding to each C_2 to C_5 alkane. The curves displayed neat maxima if T_{H_2} equalled 120 or 160°C. As well in Fig. 3 as in Fig. 4 the points represented as big circles correspond to isothermal experiments and are given for the sake of comparison.

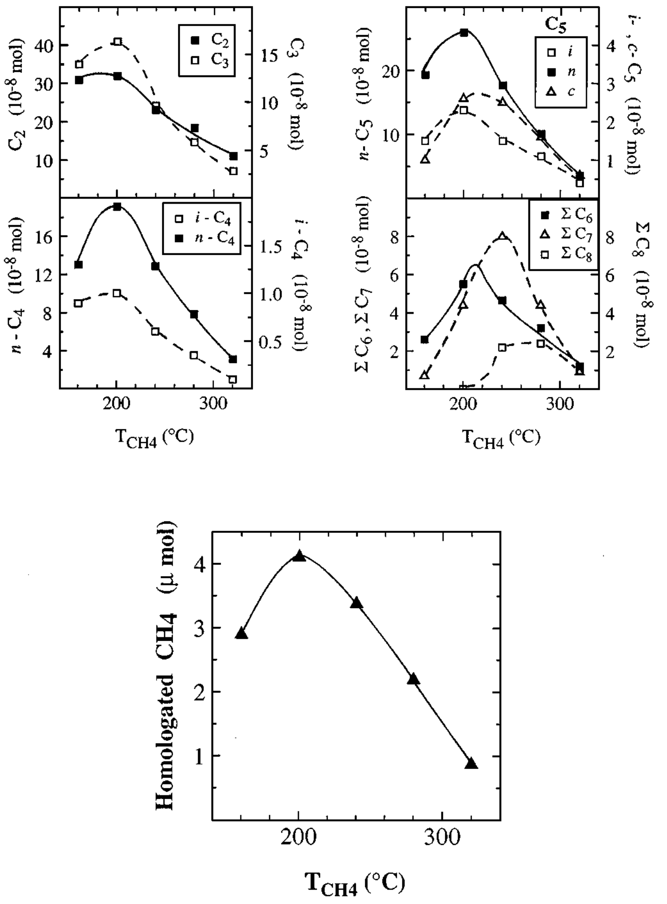

FIG. 2. Variations with T_{CH_4} of the molar amounts of the total homologated methane and of the various C_{2+} alkanes resulting from the exposure of 100 mg of **Ru/SiO₂** to methane at T_{CH_4} (step 1) and subsequent hydrogenation at a fixed T_{H_2} (120°C) (step 2). Conditions: Step 1, exposure to CH_4 (1 bar, 375 cm^3 min^{-1}; 5 min, T_{CH_4}); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, 120°C).

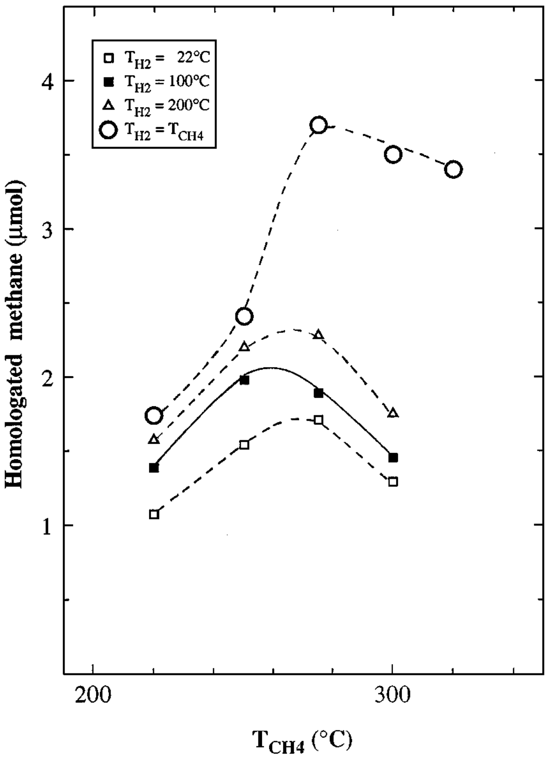

FIG. 3. Variation with T_{CH_4} of the molar amount of the total homologated methane resulting from an exposure of 100 mg of **EUROPT-1** to methane at T_{CH_4} (step 1) and subsequent hydrogenation at a fixed T_{H_2} (step 2). The different curves correspond to different values of T_{H_2}. Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 1 min, T_{CH_4}); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, T_{H_2} fixed).

1.2. Product Distributions

On Pt, there was a continuous and dramatic decrease of the selectivities to ethane and propane if T_{CH_4} was given increasing values at a fixed T_{H_2}. For example, one can see in Fig. 5, which is the bar chart corresponding to Fig. 1 (T_{H_2} = 100°C), that the selectivity to ethane decreased from ≈68 to ≈20% (while the corresponding values for propane were ≈20 and 2.6%) if T_{CH_4} was increased from 220 to 300°C. The selectivities to butanes, pentanes, and hexanes exhibited maxima. For instance, ≈21% of the homologated CH_4 was involved in hexanes at $T_{CH_4} = 275$°C. The selectivities to heptanes and octanes increased regularly up to 21.6% at $T_{CH_4} = 300$°C.

On Ru, when T_{CH_4} was given increasing values at a fixed T_{H_2}, the selectivities to ethane and propane first decreased, displayed a minimum, and then re-increased. For instance, in the case represented in Fig. 6, which is the bar chart corresponding to Fig. 2 ($T_{H_2} = 120$°C), the selectivity to ethane decreased from ≈21% ($T_{CH_4} = 160$°C) to 13.5% ($T_{CH_4} = 240$°C) and re-increased to ≈25% ($T_{CH_4} = 320$°C). The selectivity to the butanes decreased slowly throughout the range of variation of T_{CH_4}, whereas that to the pentanes decreased monotonically from ≈38% ($T_{CH_4} = 160$°C) to ≈26% ($T_{CH_4} = 320$°C). The selectivity to the hexanes underwent little changes while the selectivity to the heptanes exhibited a maximum (≈17% to heptanes at $T_{CH_4} = 240$°C). The octanes did not appear at 160 and 200°C and represented ca 10% at 280 and 320°C.

A remarkable point of these results (as of all our previous results) is that they exhibit strong departures from Anderson–Schultz–Flory (ASF) distribution. For example, after an initial exposure of Pt to CH_4 at 275°C, more CH_4 was involved in the formations of hexanes, heptanes, and octanes than in that of propane and butanes. On Ru, the same was true for the pentanes, as compared to ethane, propane, and butanes at any of the temperatures of Fig. 6. The same trends and strong departures from ASF distribution could be observed at any T_{H_2}, including r.t., as is shown by the bar charts represented in Figs. 7 and 8, corresponding to hydrogenations carried out at r.t. on Pt and Ru, respectively.

2. Results of Typical H_2-TPSRs Following Exposures to CH_4

In order to check whether C_γ was present or not after the exposures of our catalysts to CH_4 in the conditions

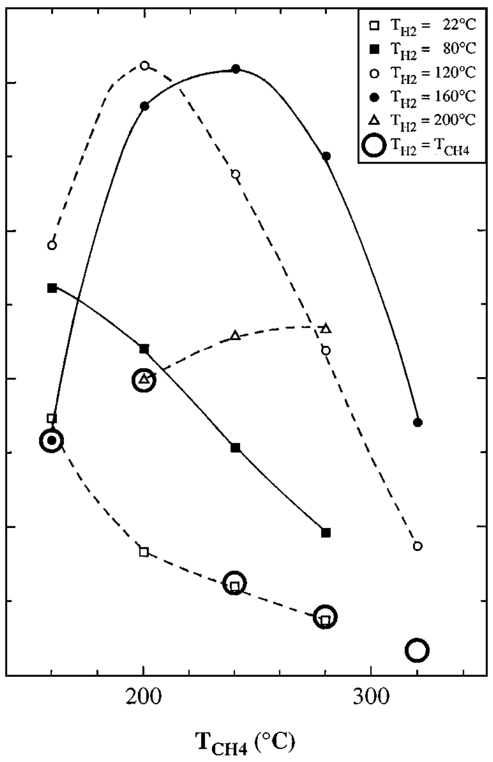

FIG. 4. Variation with T_{CH_4} of the molar amount of the total homologated methane resulting from an exposure of 100 mg of **Ru/SiO₂** to methane at T_{CH_4} (step 1) and subsequent hydrogenation at a fixed T_{H_2} (step 2). The different curves correspond to different values of T_{H_2}. Conditions: Step 1, exposure to CH_4 (1 bar, 400 $cm^3 \cdot min^{-1}$, 5 min, T_{CH_4}); Step 2, exposure to H_2 (1 bar, 50 $cm^3 \cdot min^{-1}$, T_{H_2} fixed).

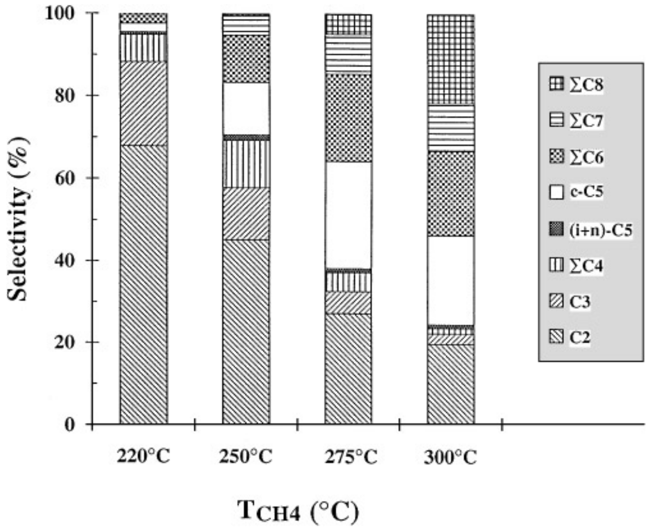

FIG. 5. Pt—Distribution of the homologated CH_4 in the C_{2+} products for various T_{CH_4}, T_{H_2} being fixed at 100°C. Data are deduced from Fig. 1.

chosen for our experiments, we have carried out H_2-TPSR's in the same way as that commonly used by other authors, that is to say without preliminary TPD's as we previously did (21, 22). Examples of such spectra are given in Figs. 9 and 10. Application of the heating program was preceded by a period of isothermal hydrogenation at r.t. (Figs. 9a, 9b and Figs. 10a) or at 100°C (Fig. 10b). The total C_{2+} productions resulting from these isothermal parts of the hydrogenations at r.t. are given in Figs. 3 and 4. Figures 9 and 10 only illustrate the profiles of CH_4 and also of C_2H_6 and C_3H_8 which could accompany the release of methane and could be chromatographically monitored on line during the heating program. For the sake of brevity, we only report the profiles corresponding to two experiments concerning each catalyst. In the case of Pt, we have chosen two exposures carrried out under the conditions here explored. Figure 9 shows how much the details of the profiles are sensitive to the temperature of the exposure. As concerns Ru, we have compared a profile generated by one of the present conditions with one corresponding to an elevated T_{CH_4} (460°C) and a low pressure of CH_4 (0.007 bar).

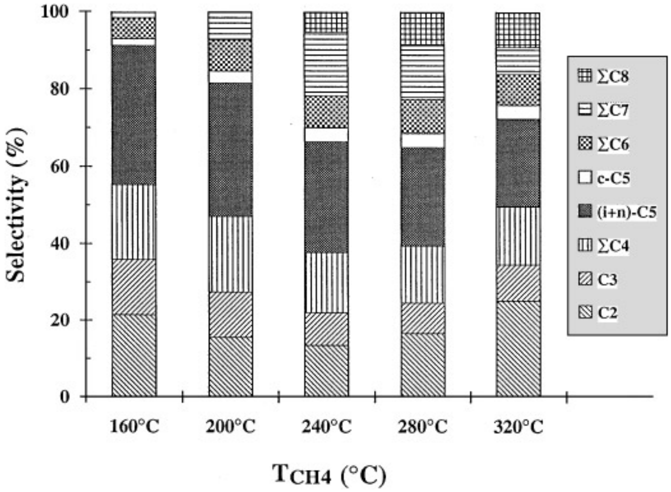

FIG. 6. Ru—Distribution of the homologated CH_4 in the C_{2+} products at various T_{CH_4}, T_{H_2} being fixed at 120°C. Data are deduced from Fig. 2.

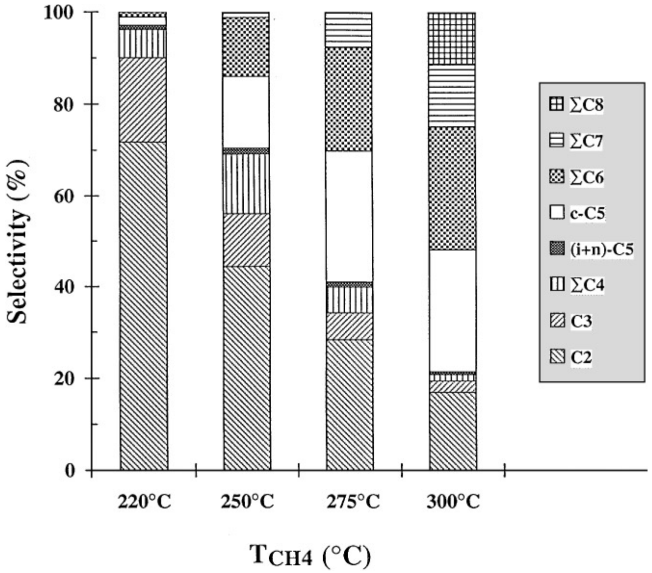

FIG. 7. Pt—Distribution of the homologated CH_4 in the C_{2+} products for various T_{CH_4}, T_{H_2} being fixed at r.t. (other conditions being the same as for Fig. 5).

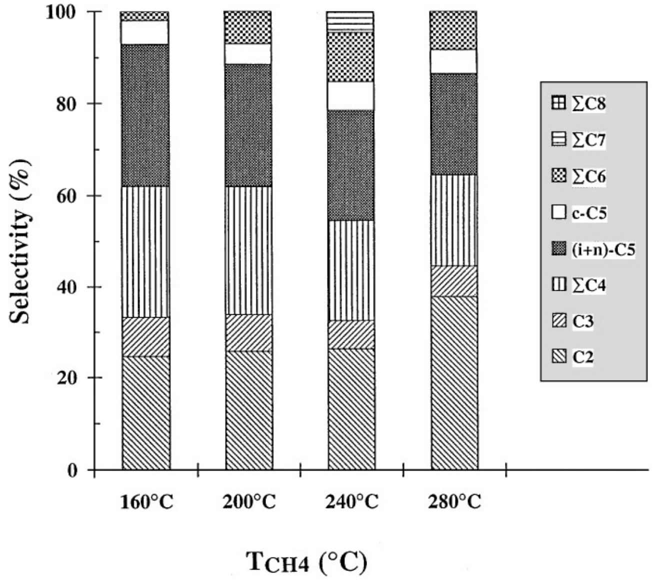

FIG. 8. Ru—Distribution of the homologated CH_4 in the C_{2+} products at various T_{CH_4}, T_{H_2} being fixed at r.t. (other conditions being the same as for Fig. 6).

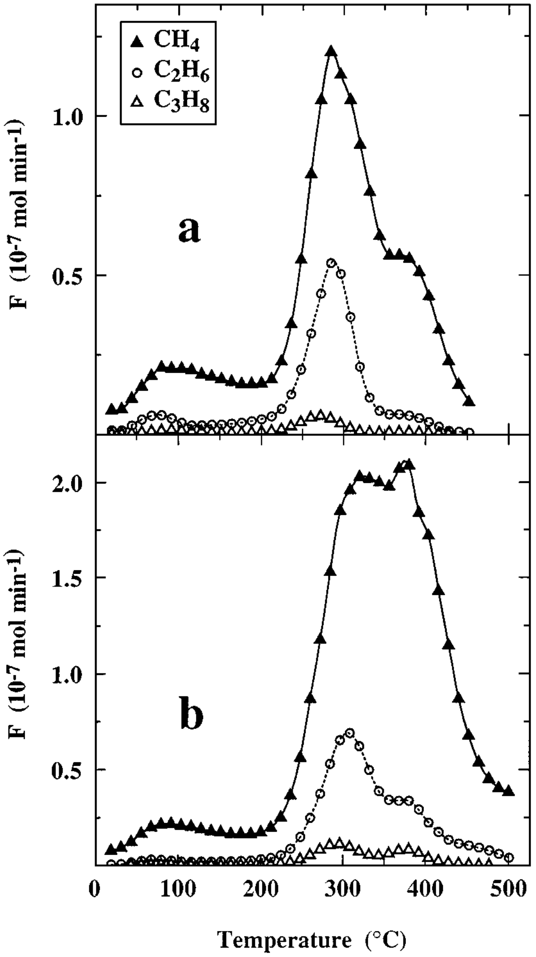

FIG. 9. H_2-TPSR of the carbonaceous species remaining on 100 mg of **EUROPT-1** after pre-adsorption of CH_4 at 250°C (a), or 300°C (b), followed by hydrogenation at r.t. Conditions: Adsorption of CH_4: 1 bar, 400 cm^3 min^{-1}, 1 min, 250°C (a), or 300°C (b). Isothermal hydrogenation: 1 bar, 50 cm^3 min^{-1}, 15 min, r.t. H_2-TPSR: 1 bar, 50 cm^3 min^{-1}, 8 K min^{-1}.

Figure 10 clearly puts into evidence how the high-temperature part of the spectrum dramatically differs when the exposure to CH_4 has been conducted under conditions allowing a large extent of CH_4 decomposition.

DISCUSSION

As T_{H_2} was most often sufficiently low for allowing us to neglect the hydrogenolysis processes, only the differences concerning the content of the adlayer built up during the exposure to CH_4 were responsible for those affecting the subsequent hydrocarbon release.

Only on Ru, did the C_{2+} production display a maximum versus T_{H_2} at a fixed T_{CH_4} (1). In the reverse present case, both metals display a maximum concerning as well the total C_{2+} production as the production of each product versus T_{CH_4} at a fixed T_{H_2}.

In Figs. 1 and 2 the rising parts of the curves are obviously due to the growth of the adlayer formed when T_{CH_4} is increased. The following decrease is much more surprising. At first sight we might consider that, if T_{CH_4} is increased, increasing amounts of unreactive carbon are formed on the catalysts, partly at the expense of reactive adspecies. However, the H_2-TPSR spectra (Figs. 9a, 9b, 10a) show that no C_γ was formed in our experiments. Moreover, if formation of C_γ was the reason of the decrease of the production of the higher alkanes, we would not have observed an increase of the latter total production upon hydrogenation at 100°C on Pt or 80°C on Ru, as compared to that at r.t., as shown in Figs. 3 and 4 since C_γ is not reacted at so low temperatures.

Due to the increase of T_{CH_4}, increasing concentrations of carbonaceous deposits are present on the surface at the

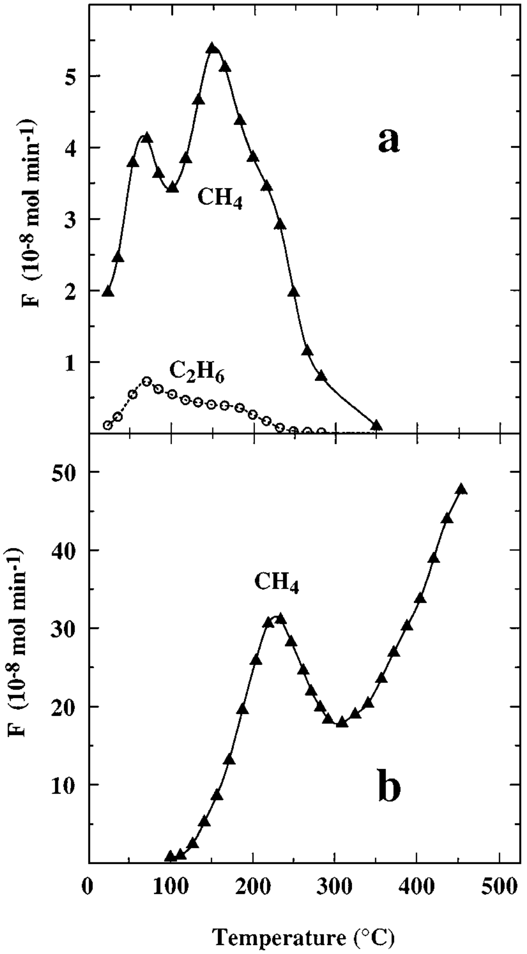

FIG. 10. H_2-TPSR of the carbonaceous species remaining on 100 mg of **Ru/SiO₂** after pre-adsorption of CH_4 at 260°C (a), or 460°C (b), followed by an isothermal hydrogenation at r.t. (a), or at 100°C (b). Conditions: Adsorption of CH_4: (a) CH_4, 1 bar, 400 cm^3 min^{-1}, 5 min, 260°C; (b) (99.3% He, 0.7% CH_4), 1 bar, 50 cm^3 min^{-1}, 20 min, 460°C. Isothermal hydrogenation: (a) 1 bar, 50 cm^3 min^{-1}, 10 min, r.t. (b) 1 bar, 50 cm^3 min^{-1}, 15 min, 100°C. H_2-TPSR: 1 bar, 50 cm^3 min^{-1}, 8 K min^{-1} (a) or 10 K min^{-1} (b).

end of the exposure to CH_4. Higher concentrations are expected to favor association through C–C bonding but the reverse may also result from increased temperatures. Contrasting situations may then prevail, depending on whether the first or the second trend is predominant. Nevertheless both of them can give rise to a maximum of the C_{2+} production versus T_{CH_4}. That the second possibility can do so is obvious. Even if less obvious, the first one can also do the same. As seen in our preceding article (1), not all the heavy precursors are removed at a low or moderate T_{H_2} during the limited duration of the hydrogenation step. Increasing proportion of heavy precursors in the adlayer makes the latter less easily retrievable during the second step of the process and can thus also explain the progressive decrease of the C_{2+} amount.

We think that a growing association versus T_{CH_4} is predominant in the case of Pt. The tendency of the platinum surface to allow the formation of heavy precursors at increased temperatures of exposure to methane has already been evidenced in our preceding contribution (1). In agreement with that, the bar chart represented in the Fig. 5 of the present contribution evidences a strong decrease of the fraction of the converted methane involved in the ethane upon increasing T_{CH_4}, T_{H_2} being fixed at 100°C. As C_2H_6 is easily removed from the surface this decrease can only result from that of its C_2 precursor among its accompanying adspecies. The same takes place for the propane and the butanes but just the opposite is observed for the C_{5+} products which eventually represent more than 75% of the homologated methane. The most dramatic variations are those exhibited by the heptanes and, above all, the octanes which are nonexistent if the exposure to CH_4 is carried out at 220°C, but which represent about 25% of the homologated methane if $T_{CH_4} = 300°C$.

On the contrary, the Ru catalyst appears to illustrate that less C–C bonding tends to occur at increased T_{CH_4}. Let us first point out in the bar chart of Fig. 6 the remarkable variation of the selectivity to ethane which exhibits a minimum at $T_{CH_4} = 240°C$, T_{H_2} being fixed at 120°C. Due to the low value of T_{H_2}, hydrogenolysis is negligible and cannot be made responsible for this mode of variation which, therefore, reflects a similar variation affecting the adlayer at the end of its formation. It is reasonable to assume that the proportion of the ethane precursor first diminishes versus T_{CH_4} because a larger fraction of it is involved in the formation of heavier adspecies. At $T_{CH_4} > 240°C$, it is the reverse which holds and this cannot result but from a lesser tendency of the adspecies present on the surface to give rise to C–C bonding. The same kind of variation is observed in the case of the propane but the butanes and the pentanes display only a lowering in the range of T_{CH_4} we have explored. The proportion of the heptanes displays a variation which is just the opposite of that of the ethane since it increases first, goes through a maximum and decreases above 240°C. The initial increase is naturally due to the building up of the necessary amount of carbonaceous adspecies and is similar to that which would necessarily have been observed in the cases of the lighter adspecies if lower values of T_{CH_4} had been explored. The further decrease is ambiguous as it can be due to some lesser tendency of the lighter units to polymerize on and also to a partial conversion of C_7 to C_8 precursors since the proportion of the octanes in the products continues to increase, or to both factors. We can expect a variation of the octanes of the same type as that of the heptanes but shifted to higher temperatures which have not been explored in this work. We can also interpret the steeper decrease of the total C_{2+} production versus T_{CH_4} on Ru (Fig. 2), as compared to the corresponding one on Pt (Fig. 1), as being partially due to the assumed lessened tendency to polymerization exhibited by carbonaceous adspecies on the Ru surface if the temperature is increased.

So far, the present discussion as well as that developed in our preceding article (1) does not refer to the presence of species such as C_α, C_β, and C_γ on the catalyst, but, instead, to that of hydrocarbonaceous precursors of different weights. Figures 9a, 9b, and 10a show H_2-TPSR profiles, corresponding to Pt and Ru, respectively, and obtained after exposures of these metals similar to those used in this work. The hydrocarbons released at r.t. are not represented and we must remark that only the profiles of CH_4, C_2H_6, and C_3H_8 could be monitored since the duration of the complete chromatographic analysis was too long to allow us to monitor each product and to get the spectra of each of them. This is all the more regrettable as we know that all the hydrocarbons described in our work are evolved throughout the whole range of T_{H_2}. Complete analysis of the products contained in each sampling of the gas exiting the reactor during the heating of the catalyst requires time consuming work and needs special equipment. However, its interest prompts us to complete it in the near future. From the present profiles we can notice that, on Ru, the release of ethane paralleled that of methane (Fig. 10a). This was still more evident in the case of platinum, and even propane exhibited the same behavior (Figs. 9a and 9b). Clearly no unreactive carbon deposits *hydrogenated into methane only at temperatures higher than 400°C* were present, unless the exposure to CH_4 was carried out under conditions of temperature and pressure favoring the CH_4 decomposition (Fig. 10b).

Most of the results described in the present article and in our preceding one (1) can thus be reasonably interpreted if one assumes the existence of hydrocarbonaceous precursors of different weights and shapes at the end of the exposure to the methane, as we have done in our previous contributions (20–23). We cannot ascribe the origin of the C_{2+} products only to the deposit displaying the highest reactivity toward H_2 and frequently reported as C_α. It may even happen that the most reactive form of carbon, i.e. that able to be converted into CH_4 at r.t., be present, without it being possible to get C_{2+} products. This is the case when the catalyst is exposed to CH_4 in a static way which does not allow a sufficient removal of H_2 (21, 22). Deeper insight into the origin of the different species and the nature of their surface precursors could be supplied by detailed and *complete* H_2-TPSR spectra. Limited to the formation of CH_4 only, the H_2-TPSR profiles constitute too crude a reactivity test. This is a conclusion akin to that already expressed by Biloen and Sachtler who considered that the role of carbidic carbon in methanation and Fischer–Tropsch reactions may have been overestimated (15).

The most reactive part of the carbonaceous deposits, i.e. C_α, might consist of C_1 adspecies, while the most unreactive part, i.e. C_γ when present, is probably graphitic carbon. However, if C_α is assumed to consist of C_1 adspecies (13) we must admit that the chain growth proceeds *during* the hydrogenation step, as in Fischer–Tropsch synthesis, whence a product distribution obeying the ASF (Anderson–Schultz–Flory) distribution. This was indeed the case in the results obtained by Koerts *et al.* (13). However, in the present work (including r.t. hydrogenations), large departures from the ASF distribution were always observed. This situation is not surprising if various precursors containing numerous C−C bonds build up during the exposure to CH_4 and if, as can be reasonably expected, some of them are favored by the surface geometry (23). We must therefore admit either that C_α is not made only of C_1 adspecies or that a good part of the precursors containing several carbon atoms, and sometimes included in C_β, is as reactive as C_α. What seems important is that, in our experimental conditions, numerous carbonaceous deposits displaying a broad range of reactivity build up during exposure of the catalyst to CH_4. The lighter precursors are able to react at r.t. while the heavier ones react at much higher temperatures.

A final remark is worth making. Most of the contributions devoted to this topic only report the formation of ethane, propane, and traces of higher products, which is in sharp contrast with our results. We think that the key condition for obtaining a good proportion of higher hydrocarbons is to allow the metal surface to reach substantial coverage with adequately dehydrogenated carbonaceous adspecies. Methyl adspecies are unable to give rise to C−C bonding and only lead to CH_4 upon hydrogenation, as does graphitic carbon at much higher temperatures. Feeding the catalyst with CH_4 for a long enough period of time at a moderate temperature, at not too low a pressure, and at a flow rate ensuring an adequate removal of H_2 appears as favorite operating conditions. It is thanks to the use of such conditions that the preferential formation of C_{5+} hydrocarbons could be obtained in our work as was the case in the contribution by Guczi *et al.* (24).

CONCLUSION

Systematic study of the products formed by hydrogenating, at a given temperature, the adlayers built up on Pt and Ru upon their exposure to CH_4 at a higher temperature allows one to get significant insights into the likely composition of the adlayer and into its changes as a function of the temperature of adsorption of the methane. Several families of hydrocarbon precursors differing in their carbon content and in their shape are formed during the exposure to CH_4. Increasing the temperature of the exposure favors the formation of precursors of increasing weight on Pt, whereas, on Ru, this trend is counteracted by the opposite tendency to a lesser degree of polymerization.

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