JOURNAL OF CATALYSIS **159,** 449–457 (1996)
ARTICLE NO. 0109

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

II. Hydrogenation of the Adspecies Resulting from the 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 Vandœuvre Cedex, France

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

Hydrogenation of the adspecies formed from CH_4 chemisorption on EUROPT-1 removes a mixture of alkanes ranging from C_1 to C_6 or C_8, depending upon the conditions. Sizeable fractions of the CH_4 initially chemisorbed can be homologized in this manner. The influences of various factors (temperature, duration of exposure, flow rate of CH_4, partial pressures of CH_4 or H_2) upon the quantity of homologized CH_4 and the product distribution are reported. In particular, it is shown that, every other factor fixed, there exists an optimum temperature for homologizing methane. That results from the occurrence of the opposite hydrogenolysis reactions during the second step of each sequence. All the results can be interpreted by assuming that C–C bonding takes place between H-deficient CH_x fragments during the chemisorption step. In the second step, H_2 saturates the alkane precursors and removes them from the surface. Fresh H_2 might not be used in the second step since more H_2 than needed is evolved during the first step. The driving force of this homologization process, conducted isothermally and in the absence of oxygen, can be seen as the energy which would then be required to compress the necessary quantity of H_2 from the low partial pressure at which it is removed in the first step up to 1 bar in order to make it able to remove alkanes from platinum. © 1996 Academic Press, Inc.

INTRODUCTION

This article is the second one of a series of two articles devoted to the *oxygen-free* conversion of methane to higher alkanes through an *isothermal two-step reaction*.

In the first article (1) we recalled the strong interest in the *direct* conversion of methane into more valuable chemicals. We put the stress on the potential importance of an *isothermal two-step conversion of methane to higher hydrocarbons* as compared to the oxidative coupling, one major disadvantage of oxidative coupling being the undesirable formation of carbon oxides due to the oxidative conditions and to the high temperature at which it must be conducted. Our two-step procedure consists first in contacting methane with dispersed metal particles and secondly in hydrogenating the carbonaceous species formed on the solid surface during the first step. After having briefly reviewed what is known up to now about the chemisorption of methane on metals as well as the reactivity of the derived adspecies, the first article of this series focused on the chemisorption of methane on Pt (first step of the homologization process) and reported on the response of the catalyst to the different key factors. The catalyst is the well-defined standard EUROPT-1.

The present report is devoted to the hydrogenation of the adspecies resulting from this chemisorption. We will look at some aspects of what can be considered as the second step of an homologization process and we will show the influence of the different parameters. Discussion will include thermodynamical as well as mechanistic considerations.

EXPERIMENTAL

The catalyst and the procedures have been described in the previous paper (1).

As reported below, feeding the catalyst with CH_4 and H_2 in turn led to the fast production of alkanes, the major part of them being obtained during the first seconds of hydrogenation. In the present work, we only report on this part of the alkane production, obtained by collecting the products of the first five or six seconds of hydrogenation into a sufficiently large sampling loop (5 cm^3), allowing us to send this total amount of products to the chromatographic column. As previously done in the case of chemisorption followed by TPD and TPSR experiments, between two successive experiments the catalyst was submitted to a flow of H_2 at 400°C for 1 h in order to remove any carbonaceous residue. It was then fed with a flow of Ar (50 cm^3/min) in order to remove H_2 and finally cooled in Ar (or He) at the temperature desired for the experiment.

---

[1] To whom correspondence should be addressed.

0021-9517/96 $18.00

RESULTS

In the experiments here described, CH_4 was switched to H_2 at the end of the exposure step, the temperature being kept constant. Immediate formation of alkanes from C_1 to C_7 (or C_8, according to the conditions) resulted from the sudden feed of the surface with H_2. Among the C_{2+} alkanes, ethane was always predominant. Linear alkanes were formed preferentially but branched alkanes were also present as well as cyclopentane, cyclohexane, and small amounts of methyl-cyclopentane and methyl-cyclohexane. Most of the total alkane production was released within seconds but low concentrations of alkanes continued to be present in hydrogen for longer durations. We recall that only the fast production is here taken into account.

1. *Influence of the Temperature*

All other operating conditions kept constant, the variation against the temperature of the production of each C_{2+} species was studied from 150 to 320°C. The molar productions are represented in Fig. 1 and the distribution of the homologated CH_4 in each C_{2+} products is given by Fig. 2. The fraction of the homologated CH_4 present in each C_{2+} product has been calculated as

$$\frac{nC_n}{\sum nC_n} \times 100,$$

where C_n is the molar quantity of the corresponding C_nH_{2n+2} alkane.

The total C_{2+} production was maximum around 250–260°C. The proportion of C_2 decreased regularly throughout the temperature range from about 85% at 150°C to 39% at 320°C. The C_{6+} alkanes were observable from 200°C only and increased regularly with the temperature, so that their proportion passed beyond 16% at 320°C. At 290°C, a little more CH_4 was converted to pentanes (ca. 39%) rather than to ethane (38.3%).

Taking into account the results concerning the quantity of CH_4 adsorbed at different temperatures and at equal other conditions of exposure, it was possible to calculate the *yield* to C_{2+}, as referred to the *adsorbed methane*, for a few temperatures. The results are given in Fig. 3, where one can see that ≈ 30% of the adsorbed CH_4 was homologized at 210°C and ≈ 20% at 250°C, the temperature corresponding to the maximum homologization. Better yields could be obtained in other specially designed experiments, as will be indicated in the discussion.

2. *Influence of the Duration of Exposure*

The effect of the duration of the exposure to CH_4 was examined at 250°C and is represented in Figs. 4 and 5. For short exposures (<1 min), a sharp increase in C_2 to C_4 production is observed as exposure time is increased while only a slight increase in observed for C_{5+}. For exposures

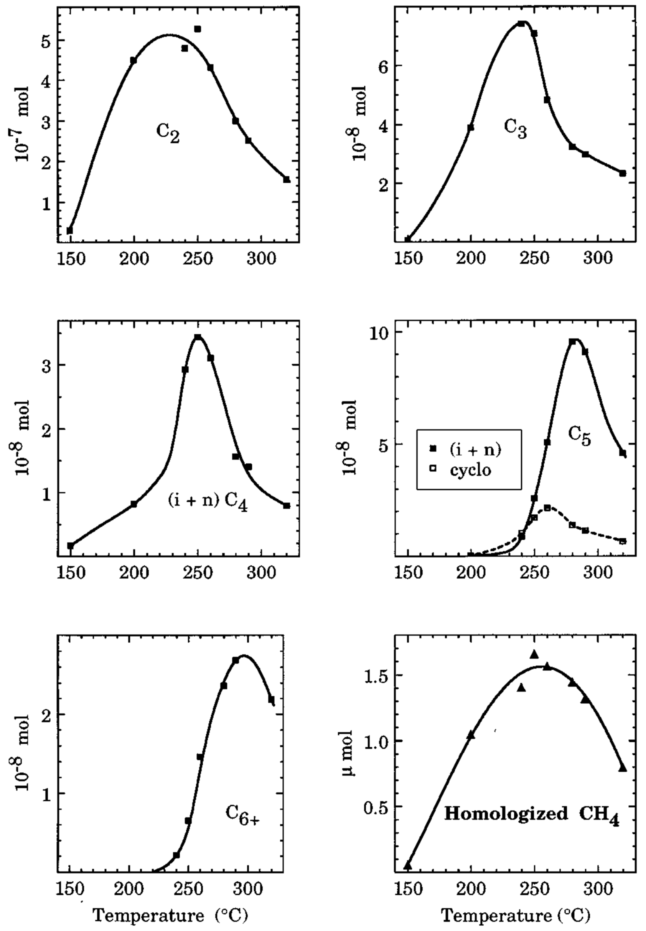

FIG. 1. Variation with temperature of the molar amounts of the total homologized methane and of the various C_{2+} alkanes resulting from exposures of 100 mg of EUROPT-1 to methane at various temperatures (step 1) and subsequent hydrogenations at the same temperature (step 2). Conditions: step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 1 min); step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}).

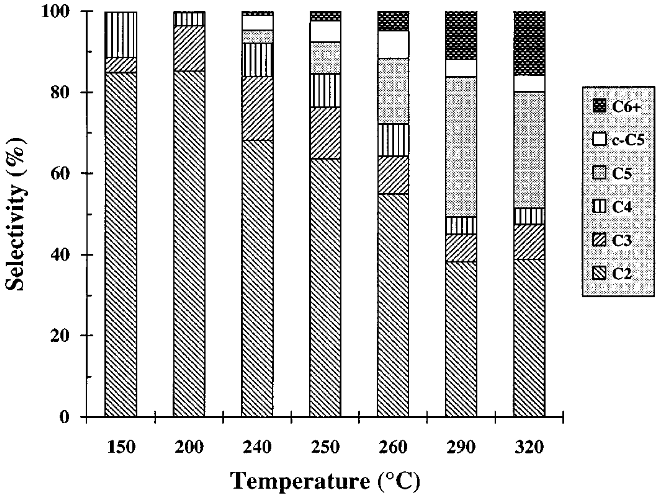

FIG. 2. Distribution of the homologized CH_4 in the C_{2+} products at various temperatures. Data are deduced from Fig. 1.

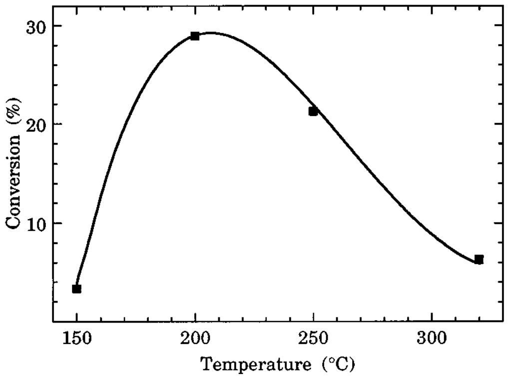

FIG. 3. Yield of conversion of the adsorbed methane to C_{2+} as a function of the temperature. Data are deduced from Fig. 1 (this article) and Fig. 4 (Ref. (1)).

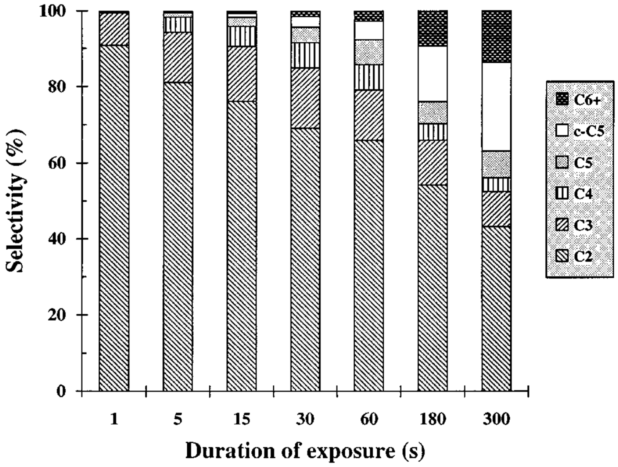

FIG. 5. Distribution of the homologized CH_4 in the C_{2+} products for exposures of various durations at 250°C. Data are deduced from Fig. 4.

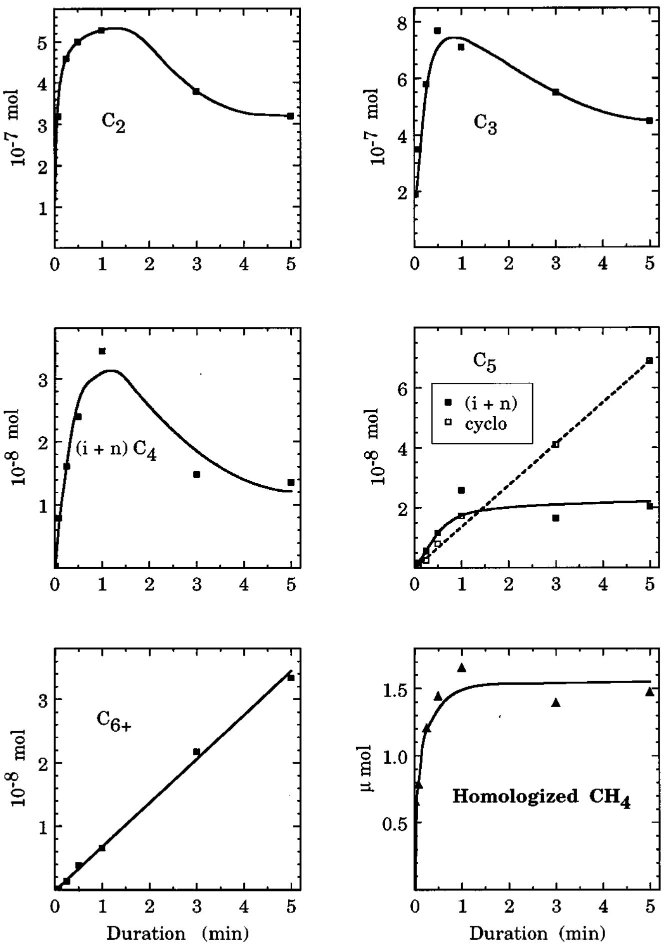

FIG. 4. Variation with the duration of the exposure to methane of the molar amounts of the total homologized methane and of the various C_{2+} products resulting from exposures of 100 mg of EUROPT-1 to CH_4 at 250°C and subsequent hydrogenations at 250°C. Other conditions are the same as for Fig. 1.

longer than 1 min, *total* C_{2+} production changes little, with the small decrease in C_2 to C_4 production being offset by the increase in C_5 and C_{6+} alkanes.

3. *Influence of the Flow Rate of Methane During the Exposure*

As there was a release of H_2 during the exposure to CH_4, the flow rate of CH_4 was expected to affect the composition of the chemisorbed layer built up at the end of a given exposure. The main features of this effect are clearly shown in Fig. 6:

(i) Very low amounts of C_{2+} alkanes were produced when the catalyst was exposed to static methane.

(ii) The total amount of each species monotonically increased with the flow rate.

(iii) Whereas the amounts of alkanes up to C_5 tended to level off, those of cyclopentane and hexanes kept on increasing and did so in an accelerated mode.

A last remark concerns the fact that the heavier alkanes were much more strengthened than the lighter ones when the flow rate was increased (increasing the flow rate from 28 to 400 cm^3/min caused less than a twofold increase of C_2 but more than a hundredfold increase of the cyclopentane and hexanes).

The vanishingly small production of C_{2+} alkanes after exposures to static CH_4 led us to close the reactor after exposure when we wanted to cool it down before a TPD. Further chemisorption of CH_4 convertible to C_{2+} products was so minimized during the fast subsequent cooling (Section 3.2 in (1)).

4. *Influence of the Methane Pressure*

The pressure of CH_4 is obviously expected to exert a strong influence on the rate of CH_4 chemisorption. This

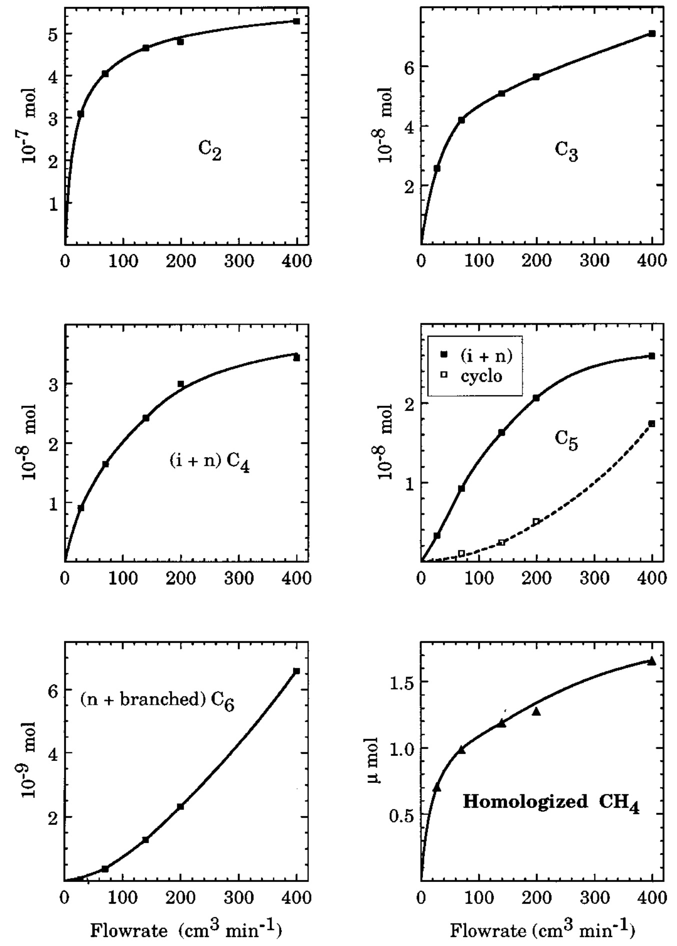

FIG. 6. Variation with the flow rate of methane of the molar amounts of the total homologized methane and of the various C_{2+} products resulting from exposures to CH_4 at 250°C and subsequent hydrogenations at 250°C. Other conditions are the same as for Fig. 1.

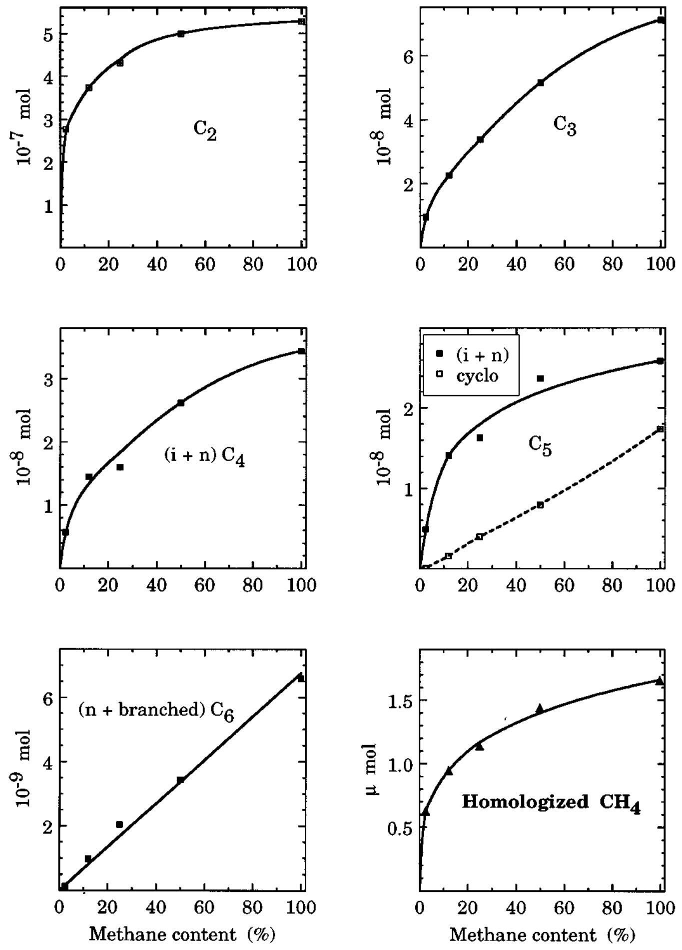

FIG. 7. Variation of the molar amounts of the total homologized methane and of the various C_{2+} products collected during the second step versus the methane content of the (He–CH_4) mixture to which the catalyst is subjected at 250°C during the first step. Other conditions are the same as for Fig. 1.

effect was studied only at CH_4 pressures lower than 1 atm by exposing the catalyst to CH_4/He mixtures at ordinary total pressure. The results of this study are presented in Fig. 7, in which one can see that the increase of each alkane production and of the total C_{2+} production versus the pressure of CH_4 looks very much like its corresponding increase versus the flow rate (Fig. 6). In view of these results it seems that not much improvement is to be expected from increasing the CH_4 pressure beyond 1 atm as regards the total C_{2+} production but a strong increase in the yield of C_5's and C_6's can be anticipated.

5. *Influence of the Hydrogen Pressure*

The last operating factor to be examined was the pressure of H_2 during the second step following a given exposure. This was done in the same way as for the pressure of CH_4, that is to say by using H_2/He mixtures. The results of this set of experiments are displayed in Fig. 8. It is to be noticed that lowering the partial pressure of H_2 has a more prononced effect than lowering the partial pressure of methane (Section 4). The higher alkanes are the most responsive to this factor. For example, decreasing the H_2 content from 100 to 50% decreases the amount of C_6 from 6.6×10^{-9} to 0.32×10^{-9} mol, and below 30% there is no C_6 left. In addition, it is to be noticed that H_2 at partial pressures equal to those prevailing in the CH_4 leaving the reactor during the first step were totally unable to release C_{2+} hydrocarbons.

6. *Effect of the Presence of Hydrogen in the Flow of Methane*

The beneficial effect resulting from increasing the flow rate of CH_4 during the first step does not seem to have another possible explanation than a more efficient removal of H_2 at higher flow rates. To check that directly we examined

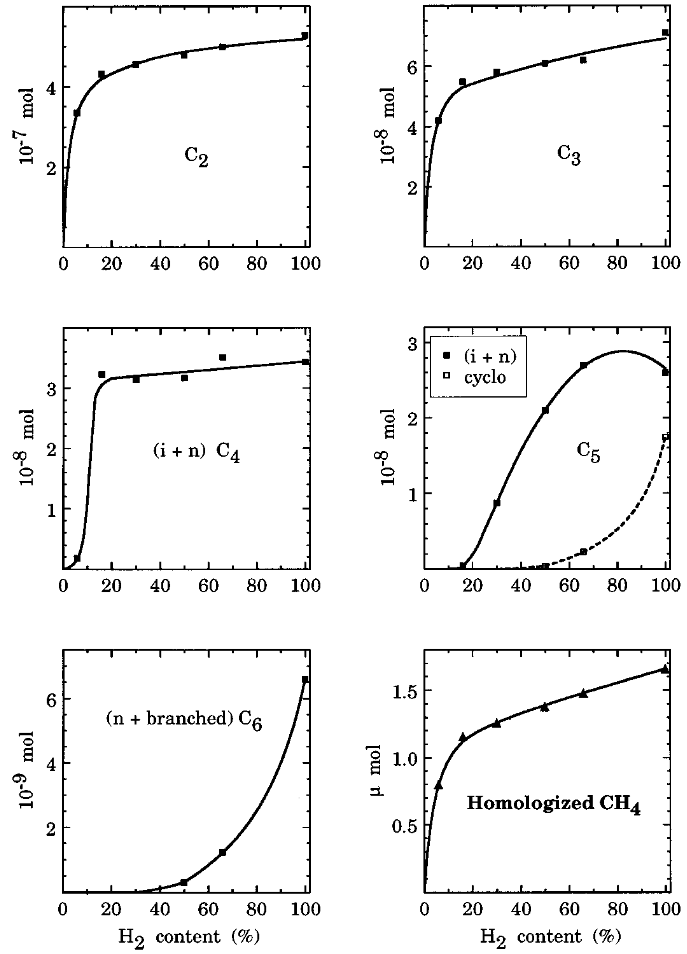

FIG. 8. Variation of the molar amounts of the total homologized methane and of the various C_{2+} products obtained at 250°C versus the H_2 content of the (Ar–H_2) mixture used in the hydrogenation step. Other conditions are the same as for Fig. 1.

what occurred when some H_2 was continuously added to the flow of CH_4 at a partial pressure averaging that of the hydrogen evolved from the catalyst during the first step. In the following hydrogenation the amount of higher alkanes was then much lower and the product distribution shifted toward the lighter products. This clearly apparent in Table 1.

7. *Repetition of Uninterrupted CH_4/H_2 Cycles*

No deactivation was observed at 250°C through subjection of the sample to a small number of cycles, each one consisting of a 1.5-min exposure to CH_4 (400 cm^3 min^{-1}) followed by a 1.5-min exposure to H_2 (50 cm^3 min^{-1}). Some deactivation became apparent after 30 cycles but heating of the catalyst in H_2 at 400°C for 15 min restored the initial activity. However, this aspect of the procedure deserves deeper examination because many more successive cycles are probably necessary to evidence some possible aging of the catalyst.

TABLE 1

Amounts of Higher Alkanes Obtained after Exposure to Methane Either Pure (A) or Containing 200 ppm of H_2 (B)

	Amount (10^{-8} mol)		
Alkane	A	B	(B)/(A)
C_2H_6	52.8	37.7	0.71
C_3H_8	7.11	3.84	0.54
C_4H_{10}	3.45	1.19	0.34
C_5H_{12}	2.60	0.54	0.21
c-C_5H_{10}	1.74	0.25	0.14
Homologized methane	166	95.7	0.57

Note. Operating conditions. Adsorption: flow rate of methane (either pure or containing 200 ppm of H_2), 400 cm^3 min^{-1}; temperature, 250°C; duration, 1 min; *p*, 1 atm. Hydrogenation: flow rate, 50 cm^3 min^{-1}; temperature, 250°C; *p*, 1 atm.

8. *Evidence for the Hydrogenolysis Activity of the Catalyst*

The decrease of the C_{2+} production beyond 250°C with other operating conditions maintained constant (Fig. 1) can reasonably be explained by the interference of the homologization process with the hydrogenolysis of the resulting alkanes.

In order to provide evidence of possible C–C bond breaking in H_2, we fed the catalyst by a mixture consisting of C_3, *n*- and *i*-C_4, *n*- and *i*-C_5, and *n*-C_6 diluted in hydrogen. The concentrations of alkanes in this mixture were similar to those formed in the reaction products ($\approx$ 2000 p.p.m. for all alkanes except for *n*-C_6, for which it was 240 p.p.m.). Consumption of *n*-hexane started at about 220°C and that of *i*- and *n*-pentane at 280°C. The concentrations of propane and butanes first increased up to 320–340°C, as they were formed from pentane and hexane, before sharply decreasing at higher temperatures.

Interference with hydrogenolysis in our two-step homologization process is all the more confirmed as the alkanes submitted to hydrogenolysis are already adsorbed on the platinum when switching to H_2.

DISCUSSION

1. *Thermodynamic Analysis*

In the whole range of temperature explored, except for the highest temperatures, the partial pressure of C_2H_6 in the flow of CH_4 leaving the catalyst during the first step of the reaction sequence remained lower than the value allowed by thermodynamics and such was the case even at maximum C_2H_6 concentration. However, when the temperature was raised at 320°C, this equilibrium value was reached under transient conditions during the first seconds of exposure.

During the first seconds of the second step, the situation was quite different. The hydrogenation occurred at a maximum rate and the resulting composition of the gas leaving the reactor varied quickly, but on-line analysis revealed concentrations of C_2H_6 which could reach several mol%. As the corresponding concentrations of CH_4 were not higher than those of C_2H_6 whereas H_2 was in large excess, one can easily calculate that the concentrations of ethane were by numerous orders of magnitude higher than the values allowed at thermodynamic equilibrium in such mixtures. The same conclusion held for the other higher alkanes. This situation calls therefore for a thermodynamic analysis.

The x values reported in the first part of this series (1) give support to successive dehydrogenation processes of the CH_x species, such as

$$CH_{3\,\mathrm{ads}} + 2* \rightarrow CH_{2\,\mathrm{ads}} + H_{\mathrm{ads}},$$

and so on. Two free active centres, rather than just one, are involved in the process since it is generally considered that the CH_x fragments tend to restore their missing bonds, CH_3 preferring the on-top, CH_2 the bridging, and CH the capping geometry (2, 3).

C–C bond formation occurs between neighboring CH_x groups but H_2 is needed to release the corresponding alkanes. That may look paradoxical since the homologization of CH_4 must yield H_2. However, we can easily check that the amount of hydrogen which was removed from the Pt sample during the first step was in all cases higher than that stoichiometrically corresponding to the subsequent C_{2+} production. For example, 9.90 μmol of H_2 was released during 1-min exposure of the catalyst to CH_4 (1 bar, 400 cm^3 min^{-1}) at 250°C. Taking the corresponding subsequent C_{2+} production into account (Fig. 1), one can calculate that the quantity of H_2 which ought to have been freed by homologization should have amounted to 1.0 μmol only. Therefore the second step has to make up for the severe dehydrogenation undergone by the carbonaceous material during the first step. However, the precursors present on the Pt surface do not require just H_2 but H_2 at a pressure much higher than that at which it was released in the first step. The work which has to be spent for the compression of the necessary quantity of H_2 is what allows the thermodynamic barrier to be overcome. We can deal with this point in a more detailed way as follows.

Focusing our attention on the case of C_2H_6 which requires association of two C_1 adspecies, the first step of our procedure can be summarized as

$$2CH_4 + 2* \rightarrow C_2H_{n\,\mathrm{ads}} + \left(4 - \frac{n}{2}\right)H_2\ \text{(low pressure)}$$

if we suppose that C_2H_n is doubly attached to the surface, whereas the second step can be written as

$$C_2H_{n\,\mathrm{ads}} + \left(4 - \frac{n}{2}\right)H_2\ \text{(1 bar)} \rightarrow C_2H_6 + 2H_{\mathrm{ads}}$$

so that the overall process is

$$2CH_4 + \left(4 - \frac{n}{2}\right)H_2\ \text{(1 bar)} + 2* \rightarrow C_2H_6 + 2H_{\mathrm{ads}} + \left(4 - \frac{n}{2}\right)H_2\ \text{(low pressure)}. \quad [A]$$

This equation expresses the material balance in the case of an initially clean surface exposed in turn to CH_4 and H_2. In a series of uninterrupted cycles, CH_4 does not contact empty sites but H-covered sites instead, and removes some of this hydrogen. More H_2 is accordingly removed from the surface than in the clean surface case and is carried away in the flow of CH_4. The balance of the first step becomes

$$2CH_4 + 2H_{\mathrm{ads}} \rightarrow C_2H_{n\,\mathrm{ads}} + \left(5 - \frac{n}{2}\right)H_2\ \text{(low pressure)},$$

and the global balance becomes

$$2CH_4 + \left(4 - \frac{n}{2}\right)H_2\ \text{(1 bar)} \rightarrow C_2H_6 + \left(5 - \frac{n}{2}\right)H_2\quad \text{(low pressure)} \quad [B]$$

In our experiments CH_4 in the first step and H_2 in the second one were used at a pressure of 1 bar. Let us assume that C_2H_6 is to be obtained at 1 bar too and let us examine whether the overall transformation is possible or not. Case [A] may be regarded as equivalent to the sum of the following three processes:

$$2CH_4\ \text{(1 bar)} \rightarrow C_2H_6\ \text{(1 bar)} + H_2\ \text{(1 bar)} \qquad \Delta G_1^0 > 0 \quad [1]$$

$$\left(4 - \frac{n}{2}\right)H_2\ \text{(1 bar)} \rightarrow \left(4 - \frac{n}{2}\right)H_2\ \text{(low pressure)} \qquad \Delta G_2 < 0 \quad [2]$$

$$H_2\ \text{(1 bar)} + 2* \rightarrow 2H_{\mathrm{ads}} \qquad \Delta G_3^0 < 0. \quad [3]$$

Case [B] does not involve neat adsorption of H_2 and is equivalent to the sum of the following two processes:

$$2CH_4\ \text{(1 bar)} \rightarrow C_2H_6\ \text{(1 bar)} + H_2\ \text{(1 bar)} \qquad \Delta G_1^0 > 0 \quad [1]$$

$$\left(5 - \frac{n}{2}\right)H_2\ \text{(1 bar)} \rightarrow \left(5 - \frac{n}{2}\right)H_2\ \text{(low pressure)} \qquad \Delta G_4 < 0. \quad [4]$$

Only in case [A] could the H_2 evolved from the surface be monitored unambiguously since, in case [B], the H_2 released from the surface was mixed up with that simply removed from the reactor. We will therefore consider case [A], which does not modify the meaning of the present approach. Common average values of the H_2 pressure during the first step occurring on an initially clean surface were lower than 5×10^{-4} bar. At 250°C this corresponds to a value of ΔG_2 (or ΔG_4) of −33 kJ/mol for each expanded mol of hydrogen. This entails that 2.14 mol of H_2 have to be expanded to compensate for the positive free energy of homologation [$\Delta G_1^0 \approx +70.5$ kJ at 250°C (4)]. We can deduce that an average value of n equal to 3.72 corresponds to $[\Delta G_1^0 + \Delta G_2] = 0$ and that lower values of n would make $[\Delta G_1^0 + \Delta G_2] < 0$. Such values appear quite reasonable if we suppose that the C_2 precursor is formed from CH_x units with x equaling 2 for very short exposures and 1 for longer ones, corresponding to n (in C_2H_n) equal to 4 or 2. Moreover, in case [A], one has also to take ΔG_3^0 into account and the whole process is therefore quite favored thermodynamically.

In case [B] the energy of adsorption does not appear explicitly but the amount of H_2 involved is higher by one mol so that the value of n making $[\Delta G_1^0 + \Delta G_4] < 0$ is equal to 5.72 and the whole process is still more favored.

Moreover, taking advantage of the absence of any adsorbed species in reaction [B], another approach can be developed. By assuming that reaction [B] is at equilibrium, the minimum H_2 pressure, $P_{H_2(\text{min})}$, which has to be used in the second step for releasing C_2H_6 at 1 bar can be derived from the law of mass action

$$K_p = \frac{[P_{C_2H_6}][P_{H_2(\text{low pressure})}]^{(5-n/2)}}{[P_{CH_4}]^2[P_{H_2(\text{min})}]^{(4-n/2)}},$$

where $[P_{C_2H_6}] = 1$ bar. The value of K_p is the same as that of the direct homologization of CH_4 to C_2H_6 since the standard free energy of reaction [B] is nothing else than the standard free energy of homologization. Taking for example $P_{H_2(\text{low pressure})} = 1 \times 10^{-3}$ bar, the minimum H_2 pressure required in the second step is 0.16 or 0.029 bar, according to whether n is, respectively, equal to 4 or 2.

Equations [A] and [B] may suggest that H_2 is one of the reactants in the procedure of homologization described here. As a matter of fact and as already indicated, more H_2 is released during the first step than is needed in the second one. Therefore no fresh H_2 is needed by our procedure on condition that the necessary quantity of H_2 be recovered from the low pressure H_2 released during the first step and that the necessary work be spent for supplying the surface precursors with H_2 at 1 bar. This is what is summarized in Fig. 9.

This analysis can naturally be easily extended to the formation of other higher alkanes. Increasing the rank of the alkane considered will increase the corresponding energy barrier but this will be balanced by the increasing quantities of H_2 involved and the corresponding increasing works which will be supplied for compressing H_2.

From Eq. [B], there is another way of completing the thermodynamic analysis. One can remark, in effect, that we only need to compress $(4 - (n/2))H_2$ instead of $(5 - (n/2))H_2$,

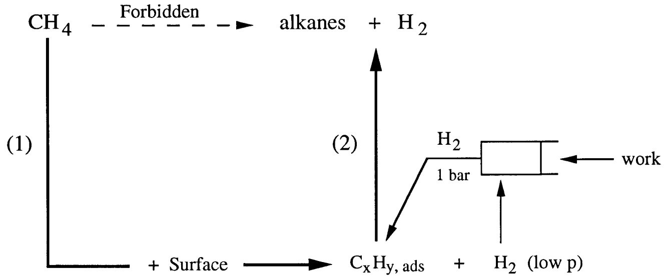

FIG. 9. Schematic representation of how the thermodynamic barrier is overcome in the isothermal two-step homologization of methane.

$$\left(4 - \frac{n}{2}\right)H_2 \text{ (low pressure)} \rightarrow \left(4 - \frac{n}{2}\right)H_2 \text{ (1 bar)}, \quad [5]$$

whereas the remaining H_2 can be considered as the desired source of energy through reaction with O_2:

$$H_2 \text{ (low pressure)} + \frac{1}{2}O_2 \rightarrow H_2O. \quad [6]$$

By adding [B], [5], and [6] we obtain a new global balance,

$$2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O,$$

which is nothing else than *oxidative coupling but without any carbon oxides formation*, since there is in fact no contact between CH_4 and O_2. Thanks to the cyclic procedure, the oxidation of H_2 could be carried out separately.

At any rate, the key point in the process is that H_2 is released at a low pressure in the first step and used at a much higher pressure in the second one. Experimental support to this view is given by several results of the present contribution:

(i) Inability of H_2, when taken at pressures equal to those prevailing in the flow of CH_4 leaving the reactor in the first step, to be used as an efficient reactant in the second step.

(ii) Increase of the total C_{2+} production with the flow rate of methane used during the first step (Fig. 6).

(iii) Increase of the total C_{2+} production, and especially of the heavier alkane production, with the pressure of the hydrogen used in the second step (Fig. 8).

(iv) Related results concerning the influence of the duration of exposure to CH_4 (Fig. 4).

Among other operating factors, the flow rate of CH_4 (with a negligible C_{2+} production after exposure in a closed reactor) is rather unexpected unless one notices that not only does the flow of CH_4 bring the reactant to the surface but, also, it removes hydrogen from the adsorbed species. Taking that into account helps us understand why no homologization was observed in previous attempts which seemed at first sight similar to ours (5). In other cases, the choice of the metal may not have been suitable for the conditions used. We thus interpret the failure suffered by Kuijpers et al. (6, 7) on Ni. We will soon report on the conditions this metal requires for allowing a significant C_{2+} formation to be reached.

We must now compare our analysis with the considerations developed by Koerts *et al.* (8, 9). At first sight our procedure appears quite similar to that used by these authors because both procedures require forced feed cycling of the catalyst. In both cases CH_4 forms an intermediate product with the metal and that product is similarly submitted to H_2. However, what is very different in the two procedures is the nature of this intermediate product. Because of the elevated temperature used by Koerts *et al.*, carbide formation was postulated by the authors. No higher alkanes could have resulted from subsequent reaction with H_2 unless the temperature was much lower, whence the requirement of a two-temperature cycle. In this respect, the approach of Koerts *et al.* is very reminiscent of that employed by Rabo *et al.* (10) when they submitted the carbon deposit resulting from the CO disproportionation on Ni, Ru, or Co, at 300°C, to H_2 doses at room temperature; some higher alkanes, up to C_4, could so be obtained.

In our case, due to the moderate temperature at which the metal is contacted with CH_4, the carbonaceous species are not totally dehydrogenated and hydrocarbonaceous species are formed on the surface. The TPSR spectra, even when obtained after previous TPDs, did not reveal the presence of unreactive C_γ so that repeated cycles could be applied successfully. Therefore the situation is quite different here from that prevailing in the experiments of Koerts *et al.* and cooling is not required before one proceeds to the second step. Although not required, cooling of the catalyst may be of interest. When this is done, at some slight extent in our case, due to our rather low temperature of exposure, the main effect observed in our study is the shift of the product distribution toward the higher alkanes because of the slowing of the interfering hydrogenolysis (11). We will soon report on this interesting aspect of the topic in a more detailed way.

2. *Mechanistic Considerations*

One major difference between the formations of C–C bonds either in the present case or in the F.T. (Fischer–Tropsch) synthesis obviously consists in the nature of the carbonaceous reactant. On the one hand, CO is a much more reactive species than CH_4 and its chemisorption can take place in parallel with that of H_2 on suitable metals. Its subsequent conversion to hydrocarbons occurs on F.T. catalysts but not on Pt since, as generally admitted, the C–O bond is not easily broken on this metal. The experiments carried out by Brady and Pettit (12) on F.T. catalysts demonstrated that C–C bonding can proceed between two CH_2 fragments and that CH_2 can serve as the building block of the surface chain lengthening. On the other hand, CH_4 is able to bring CH_x units directly to the surface of metals and we can thus explain why Pt, which is not an F.T. catalyst, can be active toward CH_4. However, in addition to commonly giving rise to a slow chemisorption process, CH_4 leads to covering of the surface with various species unable to desorb spontaneously, so that no steady state formation of higher hydrocarbons can take place. Moreover, even if this were the case, we know from thermodynamics that the homologization process would exhibit very limited extents only. After exposure to CH_4, subjection of the resulting surface to another reactant expected to dislodge some or all of the adspecies is therefore required. The present contribution illustrates what occurs with H_2 which can only give rise to alkanes.

The parallel between our reaction sequence and the F.T. synthesis requires, however, that a striking difference between both processes be underlined. A.S.F. (Anderson–Schultz–Flory) distribution, which is a well-known feature of F.T. synthesis, was repeatedly and grossly disobeyed in our experiments. For instance pentanes were more abundant than butanes (Fig. 1 shows that such was the case from 250 to 320°C; at 290°C, pentanes were ≈ 7 times more abundant than butanes). However, we must remark that A.S.F. distribution prevails in polymerization processes at steady state and when any intermediate chain has constant chances either to propagate or to terminate, irrespective of the chain length. In our case, no steady state can obviously prevail in either step. In the first step, chain lengthening occurs in parallel with the surface covering and, in the second step, all the precursors are suddenly and simultaneously submitted to H_2. Therefore, propagation and termination processes are disconnected and the products of the second step reflect the composition of the chemisorbed layer obtained at the end of the first step, although in a more or less deformed fashion due to hydrogenolysis.

A second noticeable difference between the products of CH_4/H_2 cycles and those of F.T. synthesis is that, in the cycles, branched and cyclic molecules can be formed in quite significant quantities whereas, in F.T. synthesis, normal hydrocarbons are much favored. This feature of the CH_4/H_2 cycles with respect to F.T. synthesis may originate in another deep difference between them. It is well known that, in the reacting conditions, most of the surface of a F.T. catalyst is covered with CO and the growing chains are believed to be attached by only one bond to the metal, whence normal chains are favored. In the case discussed here, only C_nH_y adspecies coming from CH_4 fragments are present on the surface and they do not compete with foreign molecules for covering the surface. Therefore nothing can prevent them from being multiply attached to the surface, whence the possible preferred formation of a given precursor as is the case on nickel for benzene (13). We suggest to find in this possibility the reason why branched and cyclic alkanes can both be formed.

3. Yields

After a preliminary adsorption of CH_4 on Pt, sizeable yields of conversion of the chemisorbed methane to higher alkanes can be reached upon further submission of the catalyst to H_2. In the preceding article (1), we have explained why the CH_4 chemisorbed on the Pt sample represented such a small fraction of the total CH_4 used. We insisted that exposure to flowing rather than to static CH_4 was necessary in order to make the adspecies sufficiently H-deficient. The results presented here show clearly how important this condition is in order to allow C–C bonding to proceed during the first step and accordingly to get homologized products in the following one. In fact, it was not our concern to obtain as good yields as possible when we carried out the reported experiments but rather to explore the potentialities of the CH_4 chemistry on metal surfaces. This chemistry has turned out to be highly responsive to the H-deficiency of the adspecies and therefore to the specific conditions of exposure.

In order to improve the yield of conversion of the incoming methane we have to use a quantity of CH_4 commensurate with the monolayer capacity of the sample. By using 1 g of EUROPT-1 this condition would be fulfilled with roughly 200 μmol CH_4, i.e., 5 cm^3 of CH_4 at ordinary conditions but provision should be made for trapping the H_2 removed from the surface as chemisorption proceeds. We have in fact put such a procedure into practice and we have shown that appreciable conversions (ca. 40%) of the total CH_4 used into higher alkanes could be reached (14, 15).

CONCLUSION

Despite its low reactivity, methane can react with platinum at moderate temperatures. On condition that the desorbed H_2 be carried away, i.e., that the exposure be done in a flow of CH_4, chemisorption of methane on platinum, above 150°C, leads to H-deficient CH_x species which can link together through a C–C bond. These hydrocarbonaceous species can be released as alkanes in the subsequent hydrogenation. An isothermal two-step reaction sequence giving rise to the homologization of CH_4 to higher alkanes is therefore possible. More H_2 turns out to be released during the first step than needed by the second step, so that the whole process is a neat producer of hydrogen. However, what allows the thermodynamic barrier to be overcome is that energy has to be spent in order to compress the necessary quantity of hydrogen set apart from the hydrogen delivered at a low partial pressure during the first step up to the suitable pressure required by the second step. The necessary quantity of energy can theoretically be supplied by oxidation of the H_2 produced in excess, which leads to a global transformation equivalent to perfectly selective oxidative homologization.

This contribution therefore illustrates the potential of metal surfaces in CH_4 chemistry, even in the absence of oxygen, a situation which avoids the formation of carbon dioxide.

ACKNOWLEDGMENT

Gaz de France is gratefully acknowledged for having supported this work.

REFERENCES

1. Belgued, M., Amariglio, A., Paréja, P., and Amariglio, H., *J. Catal.* **159**, 441 (1996).
2. Zheng, C., Apeloig, Y., and Hoffmann, R., *J. Amer. Chem. Soc.* **110**, 749 (1988).
3. De Koster, A., and van Santen, R. A., *J. Catal.* **127**, 141 (1991).
4. Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," p. 243–244. Krieger, Malabar, FL, (1987).
5. Frennet, A., *Catal. Rev. Sci. Eng.* **10**, 37 (1974).
6. Kuijpers, E. G. M., Breedijk, A. K., van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **72**, 210 (1981).
7. Kuijpers, E. G. M., Breedijk, A. K., van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **81**, 429 (1983).
8. Koerts, T., and van Santen, R. A., *J. Chem. Soc. Chem. Commun.,* 1281 (1991).
9. Koerts, T., Deelen, M. J. A. G., and van Santen, R. A., *J. Catal.* **138**, 101 (1992).
10. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53**, 295 (1978).
11. Belgued, M., Monteverdi, S., Paréja, P., Amariglio, H., Amariglio, A., and Saint-Just, J., *in* "Natural Gas Upgrading II" (G. A. Huff and D. A. Scarpiello, Eds.), Preprints of the Second International Symposium on Natural Gas Upgrading, April 5–10, 1992, A.C.S. Div. Pet. Chem., San Francisco, CA, Vol. 37, p. 324.
12. Brady, R. C., and Pettit, R., *J. Amer. Chem. Soc.* **102**, 6181 (1980).
13. Yang, Q. Y., Johnson, A. D., Maynard, K. J., and Ceyer, S. T., *J. Amer. Chem. Soc.* **111**, 8748 (1989).
14. Amariglio, A., Paréja, P., Belgued, M., and Amariglio, H., *J. Chem. Soc. Chem. Commun.,* 561 (1994).
15. Paréja, P., Amariglio, A., Belgued, M., and Amariglio, H., *Catal. Today* **21**, 423 (1994).