JOURNAL OF CATALYSIS **177,** 113–120 (1998)
ARTICLE NO. CA982082

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

1. Chemisorption of CH_4 at a Fixed Temperature

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Received October 20, 1997; revised March 2, 1998; accepted March 17, 1998

Preliminary chemisorbed on Pt and Ru at a moderate temperature (≈150–300°C), methane can be converted to higher alkanes through subsequent hydrogenation at the same temperature. On both metals too elevated temperatures must be avoided because of adverse hydrogenolysis reactions. Here we describe and discuss the results of dual-temperature experiments carried out on both metals and consisting of chemisorptions effected at a fixed temperature, T_{CH_4} ($\leq$320°C), followed by hydrogenations at a given temperature, T_{H_2}, ranging from room temperature to T_{CH_4} in a set of successive experiments. On both metals, strong favoring of the selectivity to heavier alkanes resulted from the lowering of T_{H_2}. On Pt, the total amount of homologated methane was an increasing function of T_{H_2}. Conversely, on Ru the homologated methane exhibited an optimum value versus T_{H_2}, which could largely exceed the value corresponding to an hydrogenation conducted at $T_{H_2} = T_{CH_4}$ (isothermal experiment). On both metal surfaces, heavy adspecies can grow upon exposure to CH_4 and it is suggested that the difference between the two metals has essentially to be linked to their different hydrogenolysis activities. The high hydrogenolysis activity of Ru caused the final decrease of the C_{2+} production beyond some critical value of T_{H_2}. The mediocre hydrogenolysis activity of Pt did not prevent the total C_{2+} production from monotonically increasing versus T_{H_2} in the range of temperature explored. It could even bring a positive contribution by allowing some heavy (and not easily removed) surface precursors to be cut into lighter and more quickly retrieved species.

INTRODUCTION

Aside from oxidative coupling, some successful attempts to upgrade CH_4 into higher hydrocarbons under reducing conditions have been reported in the last few years (1–13). Most of these new attempts consist of the hydrogenation of carbonaceous species built up on the surface of suitable metal catalysts during their preliminary exposure to methane and have been previously reviewed (14).

Van Santen *et al.* (2, 5) have decomposed CH_4 on Co and Ru, in particular, and have considered that higher alkanes can be obtained only if the carbide formed during the first step is reacted with H_2 at a much lower temperature. Complete decomposition of a large part of CH_4, possibly accompanied with bi-dimensional carbide formation, can reasonably be envisioned in the experiments carried out by these authors, due to the rather elevated temperatures at which the metals were contacted with CH_4 (450°C) and also due to the low pressure of CH_4 which was diluted in an inert carrier gas (0.5% or less).

However, we have shown that an *isothermal* operation is also possible on Pt, Ru, and Co at ordinary pressure insofar as complete decomposition of CH_4 in the first step as well as severe hydrogenolysis in the second step are avoided, which essentially means that the temperature must remain moderate and that low pressures of CH_4 must be avoided (1, 3, 9–11). We have already explained why the thermodynamic limitation of the homologation of CH_4 can be overcome by our isothermal cyclic procedure (10, 11, 14, 15).

Hydrogenation at a temperature lower than that of the CH_4 chemisorption may be envisioned for lessening hydrogenolysis. It is now the purpose of two successive contributions to present the results of such attempts in the case of Pt and Ru catalysts.

There are two ways of carrying out a systematic study of dual-temperature experiments:

(i) the metal surface is exposed to CH_4 at a temperature, T_{CH_4}, fixed for all the experiments of a same set. Hydrogenation of the resulting adspecies is then performed at $T_{H_2} < T_{CH_4}$, different values being ascribed to T_{H_2} in the successive experiments of the set.

(ii) Conversely, T_{H_2} can be fixed for a set of experiments, T_{CH_4} being given different values in the successive experiments.

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0021-9517/98 $25.00

In each way there can be as many sets as different possible values ascribable to T_{CH_4} in (i) or T_{H_2} in (ii). From a large number of experiments conducted on each metal we have extracted one set corresponding to the procedure (i) and we are reporting its detailed results (total C_{2+} production and product distribution) in the present contribution. Only the total C_{2+} productions are reported for other settings of T_{CH_4}. We have proceeded in a similar way in a further contribution devoted to the procedure (ii).

EXPERIMENTAL

1. Apparatus

The experiments were performed at atmospheric pressure in a flow-type apparatus already described (9).

The gases, He "U", H_2 "U", and CH_4 N45, were obtained from Air Liquide and were further purified to remove traces of O_2, CO and condensable impurities by standard procedures as already reported (9). No impurity traces could be detected in the gases by gas chromatography, which means in particular that the methane contained less than 0.1 ppm of other hydrocarbon impurities.

The gases leaving the reactor during hydrogenation were sent to a trap filled with glass beads and immersed in liquid air. All the hydrocarbons but CH_4 were collected in totality. They were subsequently analyzed by gaseous chromatography on a Porapak QS column.

2. Experimental Procedure

Between two successive experiments, the sample, either Pt or Ru, was flushed at 400°C first with H_2 for 2 h (50 cm^3/min) to remove all possible carbon residues and, second, with He or Ar (50 cm^3/min) for 15 min to remove the adsorbed H_2. The sample was then cooled under He at the temperature, T_{CH_4}, desired for the methane adsorption. T_{CH_4} never exceeded $\approx$300°C for avoiding excessive formation of unreactive carbon deposits. The conditions of the exposures to CH_4 were chosen in agreement with the results already reported (10, 11). The durations of the exposures of Ru to CH_4 (5 min) had to be longer than that of Pt (1 min) in order to get sizeable amounts of C_{5+} products (11). After having proceeded to CH_4 chemisorption and if the subsequent hydrogenation had to be carried out at a temperature $T_{H_2} < T_{CH_4}$ (dual-temperature experiments), the catalyst was quickly cooled to T_{H_2} (several tens of degrees/min), *the reactor being closed*, which made further chemisorption of CH_4 during the cooling negligible (9, 11). The reactor was then re-opened and CH_4 was switched to H_2. At $T_{H_2} > 100$°C, a good part of the removable amount of each product was removed from the surface within seconds or a few tens of seconds, according to the temperature. At lower temperatures, and particularly at room temperature (r.t.), a longer hydrogenation was required. At any temperature no C_{2+} hydrocarbons (including C_2H_6) could be detected in the effluent after 10 min, which does not mean that the product removal was completed, as will be seen in the following. The H_2 flow was however maintained for 15 min in order to evacuate the major part of the CH_4 condensed in the trap—essentially due to the purge of the reactor by H_2 after the exposure step when opening the reactor and switching CH_4 to H_2. Overlapping of the peaks of CH_4 and C_2H_6 was so avoided in the further analysis.

3. Catalysts

The catalysts used in the present study are of the same nature as those having given rise to former reports (9–11), namely:

(i) EUROPT-1, a Pt catalyst from the "Eurocat" group (16–19), made of silica-supported Pt (6.3 wt%). Based upon 105 μmol H_2 chemisorbed dissociatively per gram of catalyst at r.t. and assuming 1 : 1 stoichiometry, the dispersion of Pt has been estimated as being equal to 65% (18). Accordingly, about 21 μmol of surface Pt atoms were present on our 100 mg sample after reduction performed as previously (9).

(ii) a silica supported Ru catalyst (4.7 wt%), prepared and reduced as previously reported (11). Its dispersion was estimated as being equal to 36%, which corresponds to about 17 μmol of surface Ru atoms being present in our 100 mg sample after reduction.

RESULTS

Before reporting on the dual-temperature experiments, it seems useful to recall the results of reference isothermal experiments.

1. Reference Isothermal Experiments

As already reported (10, 11), each metal submitted to isothermal experiments led to a total C_{2+} production exhibiting a maximum versus temperature, as can be seen in Figs. 1 and 2. This was easily interpreted as the result of the interference of hydrogenolysis reactions with the hydrogenation/desorption of adsorbed C_{2+} precursors. We will come back later on the case of Pt because of the much slower decrease of the amount of the total homologated methane beyond the maximum, as compared to that corresponding to Ru. One can even notice a re-increase of the C_2–C_4's above 300°C.

Contrasting results were obtained on Pt and Ru concerning the product distributions. Lighter hydrocarbons were favored on Ru when increasing the temperature (11), whereas the reverse held on Pt up to 300°C (10).

2. Dual-Temperature Experiments (Fixed T_{CH_4})

In a series of experiments corresponding to a fixed T_{CH_4}, while different values are ascribed to T_{H_2} in the successive

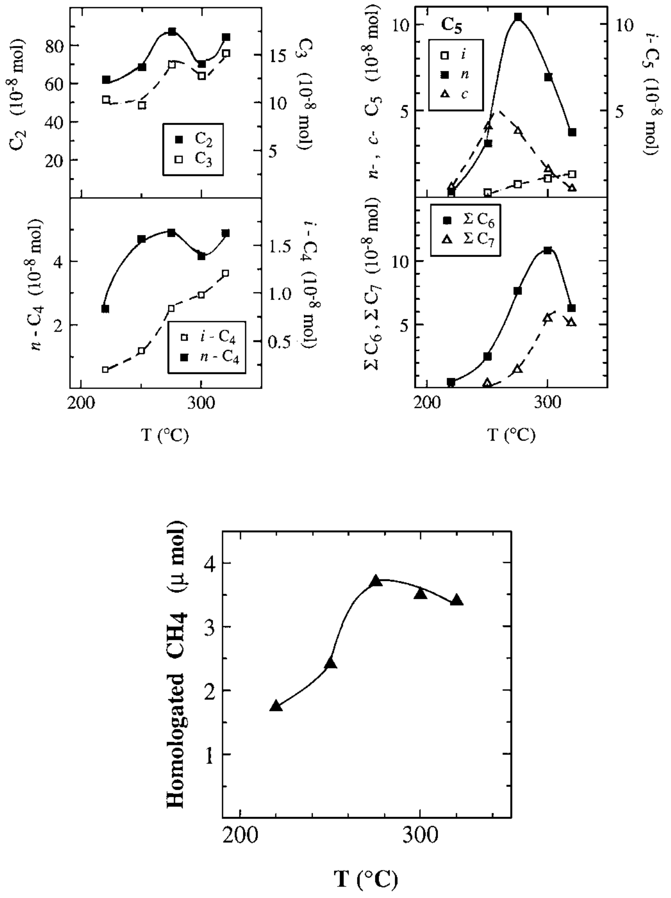

FIG. 1. Variations with temperature of the molar amounts of the total homologated methane and of the various C_{2+} alkanes resulting from exposures of 100 mg of **EUROPT-1** to methane (step 1) and subsequent hydrogenations (step 2). Both steps are carried out at the same temperature. Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 1 min, T); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, T).

experiments, it is clear that the same adlayer is involved in each experiment. Results appeared to be quite different on Pt and Ru, regarding as well the variation of the total C_{2+} production as that of the product distribution. The most salient features of the results are described below.

2.1. *Total C_{2+} Productions*

Concerning Pt, the set of experiments relative to $T_{CH_4} = 300°C$ can be taken as an example of all the experiments of the kind considered here. One can see in Fig. 3 that the total amount of homologated CH_4 decreased monotonically when the temperature of the second step was assigned decreasing values in the successive attempts and attained a slowly decreasing value if $T_{H_2} < 100°C$. All the products exhibited the same kind of variation, except for cyclo-pentane and the sum of the octanes. For a large part the increase of c-C_5 when T_{H_2} was decreased corresponded to the opposite variation of n-C_5, so that the total amount of pentanes was nearly invariant with respect to T_{H_2}. For the sake of brevity, only the *total* amounts of homologated CH_4 which resulted from similar experiments corresponding to exposures at other fixed T_{CH_4} values (220, 250, 275°C) are collected in Fig. 4, where the results of the isothermal experiments are also represented (big empty circles) to make the comparisons easier. At each fixed T_{CH_4}, the homologated matter recovered when the hydrogenation was performed at r.t. remained an important part of the homologated matter obtained in the isothermal experiment.

Contrasting with the preceding monotonic variations of the total C_{2+} productions on Pt, neat maxima were obtained in the corresponding experiments on Ru, so that dual-temperature experiments could result in a strong increase of the homologated CH_4 when T_{H_2} was decreased. This is illustrated in Fig. 5 relative to the example of $T_{CH_4} = 240°C$. In this case, the total production was roughly eight times higher when the hydrogenation was effected at 160°C (dual-temperature experiment) instead of 240°C (isothermal experiment) and the total homologated matter retrieved at

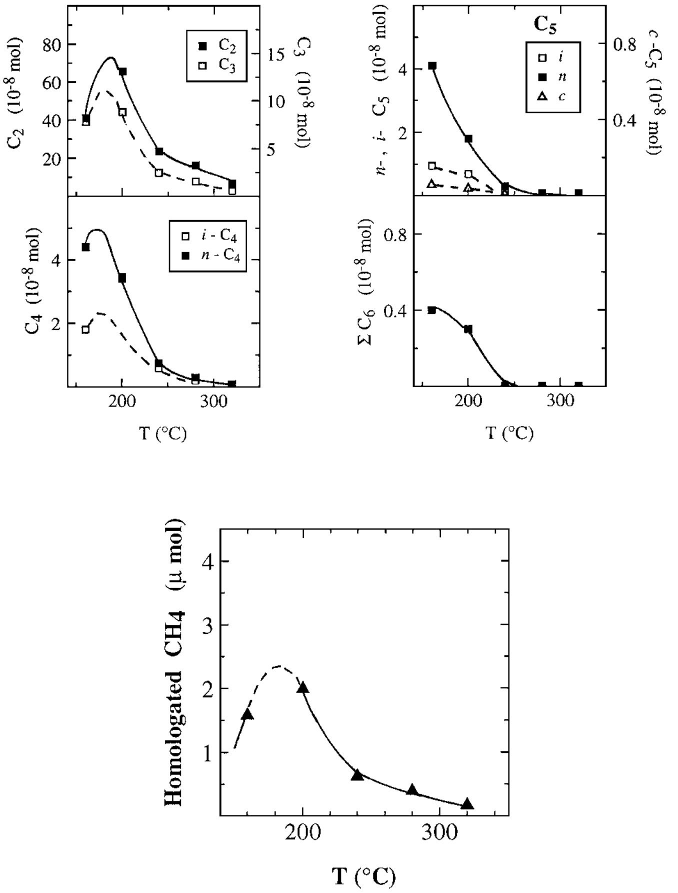

FIG. 2. Variations with temperature of the molar amounts of the total homologated methane and of the various C_{2+} products resulting from exposures of 100 mg of **Ru/SiO$_2$** to methane (step 1) and subsequent hydrogenations (step 2). Both steps are carried out at the same temperature. Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 5 min, T); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, T).

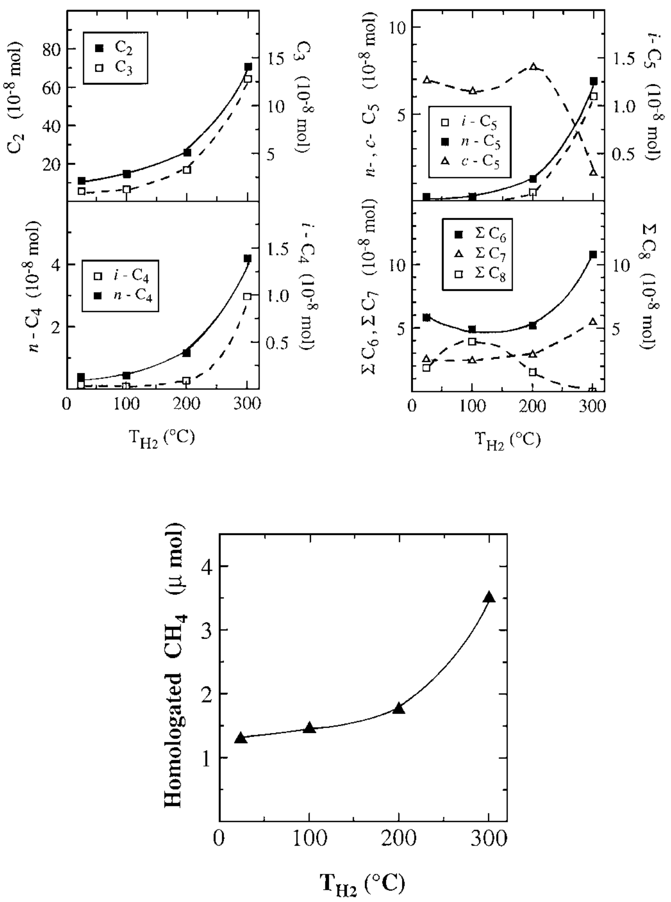

FIG. 3. Variations with T_{H_2} of the molar amounts of the total homologated methane and of the various C_{2+} alkanes resulting from a given exposure of 100 mg of **EUROPT-1** to methane at a fixed T_{CH_4} (step 1) and subsequent hydrogenation at T_{H_2} (step 2). Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 1 min, $T_{CH_4} = 300°C$); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, $T_{H_2} \leq T_{CH_4}$).

r.t. amounted to nearly the same value as in the isothermal experiment. All the products showed the same kind of variation versus T_{H_2} as the total homologated methane and exhibited a maximum between 100 and 200°C. Here again only the total amounts of methane homologated in similar experiments corresponding to other values of T_{CH_4} are represented in Fig. 6 which also displays the isothermal runs to make comparisons easier. All the curves of Fig. 6 have the same aspect as the curve related to $T_{CH_4} = 240°C$ and put into evidence that approximately the same amount of homologated matter is retrieved when the hydrogenation is performed at r.t. instead of T_{CH_4}.

2.2. Product Distributions

It is now useful to focus on the product distribution which also displayed strikingly different behaviors on both metals. To this end, we here define the selectivity to a higher alkane as the percentage of the total *homologated* CH_4 which has been involved in its formation.

Figure 7, related to Pt, is the bar chart corresponding to Fig. 3. It displays two opposite and complementary trends concerning the C_2–C_4 hydrocarbons and the C_{5+} hydrocarbons, respectively. The global proportion of CH_4 involved in the formation of ethane, propane, and butanes increased with T_{H_2} and attained 57% at $T_{H_2} = 300°C$ and, consequently, the proportion of CH_4 involved in the C_{5+} hydrocarbons obeyed an opposite variation as it decreased from 78 to 43% when T_{H_2} increased from r.t. to 300°C. More than 50% of the converted methane was present as *c*-pentane plus hexanes if the hydrogenation was carried out at r.t. Strikingly the octanes, nonexistent if $T_{H_2} = 300°C$, represented ca 22% of the homologated methane if T_{H_2} was decreased to 100°C. However, it must be kept in mind that, if T_{H_2} was made higher, despite a decreasing *selectivity* to the heavier products there continued to be an increase of the *amounts* of the latter products. For instance, the quantity of hexanes grew by about 85% when T_{H_2} was 300°C instead of r.t.

Contrasting with what was observed on Pt, the selectivity to C_2–C_4 alkanes displayed by Ru began by decreasing

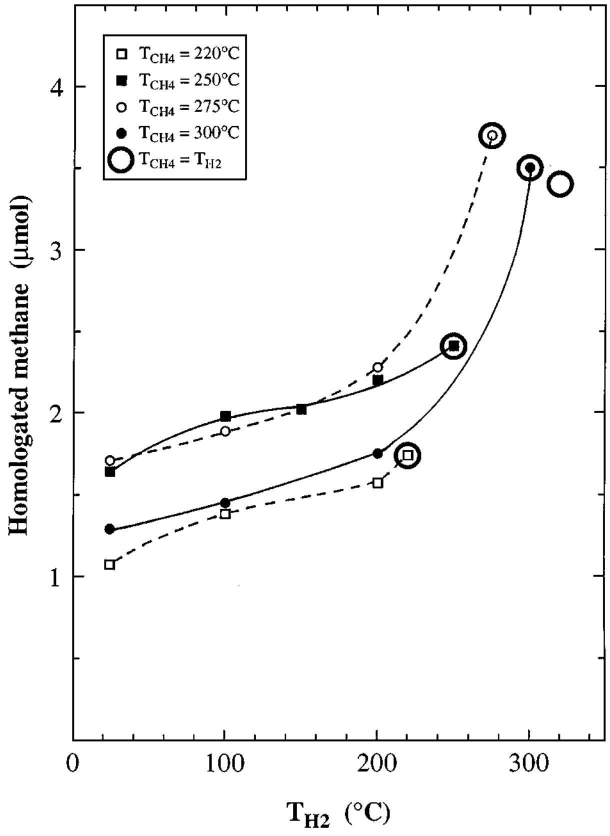

FIG. 4. Variation with T_{H_2} of the molar amount of the total homologated methane resulting from a given exposure of 100 mg of **EUROPT-1** to methane (step 1) and subsequent hydrogenation at T_{H_2} (step 2). Each curve corresponds to a given value of T_{CH_4} (step 1). Conditions: Step 1, exposure 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}, $T_{H_2} \leq T_{CH_4}$).

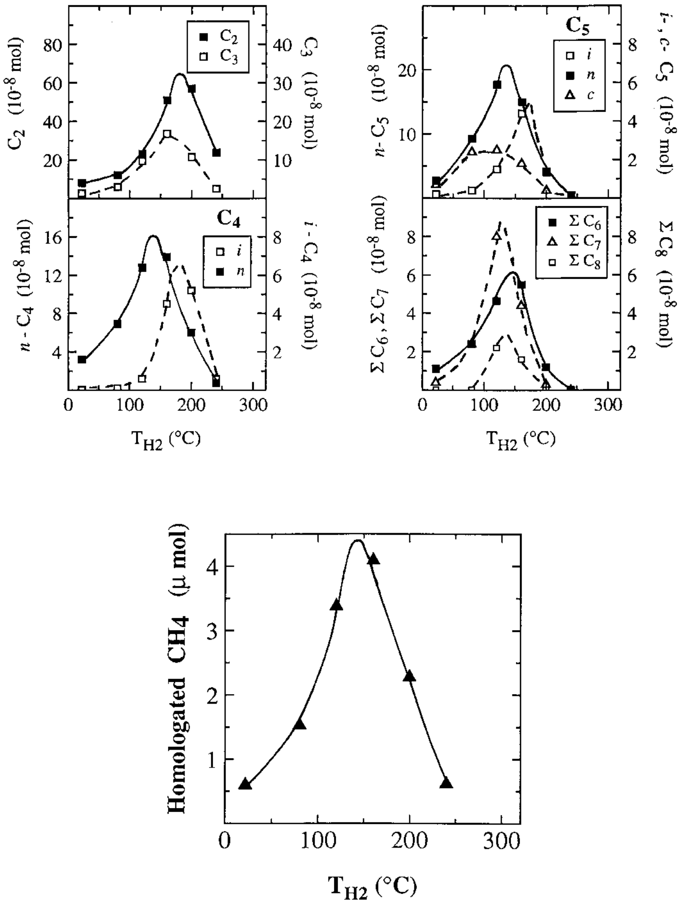

FIG. 5. Variations with T_{H_2} of the molar amounts of the total homologated methane and of the various C_{2+} alkanes resulting from a given exposure of 100 mg of **Ru/SiO2** to methane at a fixed T_{CH_4} (step 1) and subsequent hydrogenation at T_{H_2} (step 2). Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 5 min, $T_{CH_4} = 240°C$); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, $T_{H_2} \leq T_{CH_4}$).

when T_{H_2} was given increasing values before strongly reincreasing at $T_{H_2} \geq 160°C$ (Fig. 8). An opposite variation affected the selectivity to the C_{5+}'s and particularly to n-C_5. On this metal, not only could the total homologation be increased due to the lowering of T_{H_2} but, also, the selectivity to the heavier products could follow a similar trend. In the experiment taken as an example, it was to n-pentane that the selectivity was maximum at $T_{H_2} = 80$ or 120°C. Even in terms of molar quantities the pentanes as a whole were the most abundant product if $T_{H_2} = 80°C$ and there were near equal molar quantities of ethane and pentanes if $T_{H_2} = 120°C$.

2.3. Yields

In our previous contributions we have reported how much of the CH_4 chemisorbed on Pt or Ru was converted to C_{2+} products under specific isothermal operating conditions. Dual-temperature experiments as those reported in the present work deeply affect as well the yields as the product distributions, as can easily be seen from direct comparaisons between the two sets of data. In the case of Pt, due to the lessening of the C_{2+} production caused by the decrease of T_{H_2}, lower yields are obtained while the reverse is true for Ru. In the latter case, conversions higher than 70% can be obtained. In both cases, a good choice of T_{H_2}, with respect to a given T_{CH_4}, can result in a large shift of the distribution toward the heavier products.

DISCUSSION

Before going into the detailed discussion of the results we have to comment upon the performances of our catalysts which appear to be somewhat different from those previously reported (10, 11). As we have already explained, good reproducibility is displayed by the catalysts in an uninterrupted series of experiments not exceeding a few days. However, repetition of a large number of runs during several weeks results in progressive changes of the activity level with no true qualitative modification of the catalyst

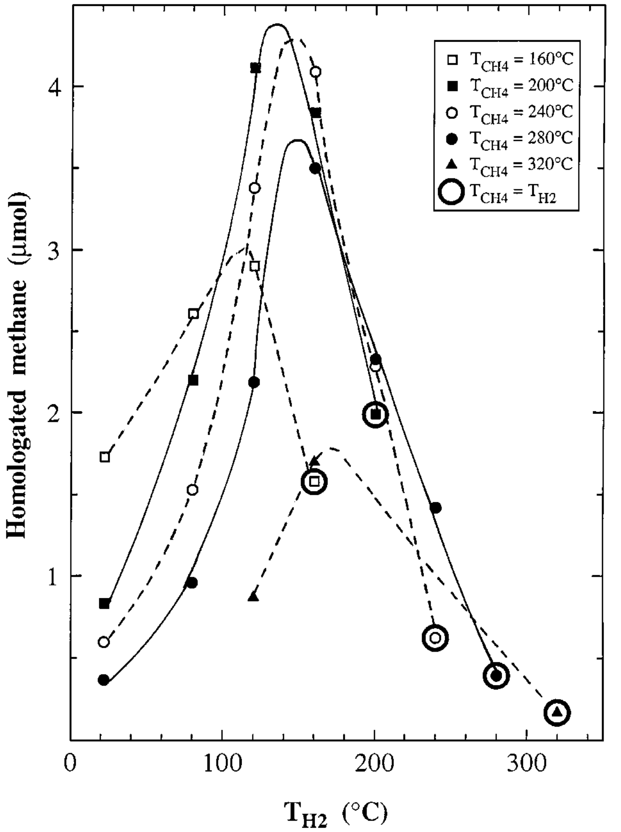

FIG. 6. Variation with T_{H_2} of the molar amount of the total homologated methane resulting from a given exposure of 100 mg of **Ru/SiO2** to methane (step 1) and subsequent hydrogenations at T_{H_2} (step 2). Each curve corresponds to a given value of T_{CH_4} (step 1). Conditions: Step 1, exposure to CH_4 (1 bar, 400 cm^3 min^{-1}, 5 min, T_{CH_4}); Step 2, exposure to H_2 (1 bar, 50 cm^3 min^{-1}, $T_{H_2} \leq T_{CH_4}$).

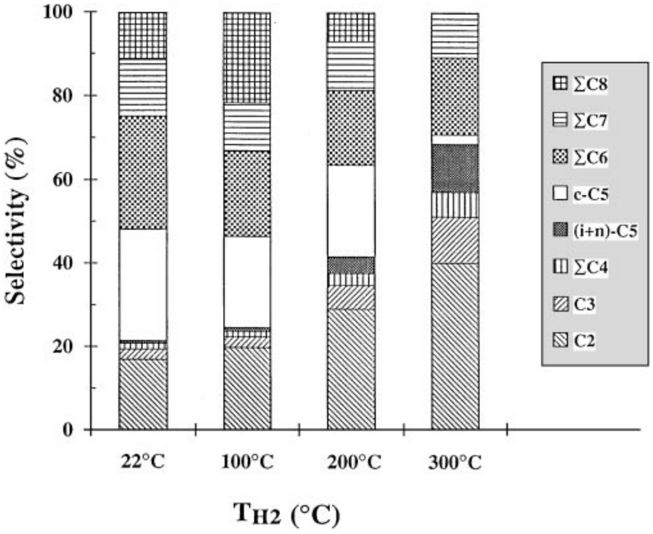

FIG. 7. **Pt**—Distribution of the homologated CH_4 in the C_{2+} products at various T_{H_2}, T_{CH_4} being fixed at 300°C. Data deduced from Fig. 3.

behavior. In the present studies, the Pt catalyst was a fresh sample, whereas the previous results (9, 10) referred to a sample having been used for weeks. Just the reverse holds concerning the Ru samples. This is the reason why the present levels of activity of the Pt catalyst are higher than those reported previously while those given by the Ru catalyst are lower than those reported in (11). Let us now discuss the results themselves.

Chemisorption of methane under fixed conditions is expected to result in the formation of a given set of surface oligomers which are the precursors of the hydrocarbons produced during the subsequent hydrogenation. In the latter process the H-deficient precursors must be adequately supplied with H_2 for desorbing (10, 11). A reliable representation of the adlayer content in precursors of different weights could be attained through the distribution of the final C_{2+} products if all the adspecies could be removed by H_2 with no other chemical changes than just hydrogenation.

We will soon report on the results of a study devoted to the kinetics of the hydrogenation step. It will be shown that, for each metal, at temperatures close to that corresponding to the maximum isothermal production (ca 250 and 160°C for Pt and Ru, respectively), more than 50% of the total C_{2+} production can be retrieved in a few seconds, whereas the rest of the adspecies requires much longer times (several minutes), so that the duration of 15 min may become quite insufficient for retrieving a significant part of the adlayer if the temperature of the experiment is decreased. In the dual-temperature experiments reported here, the temperature of hydrogenation, T_{H_2}, is always lower than the temperature of exposure to methane, T_{CH_4}. When T_{H_2} is given decreasing values, the hydrogenation process slows down, particularly at the lowest T_{H_2} values lying between r.t. and ca 100°C, so that only a part of the adlayer can be retrieved at such temperatures. We must furthermore remark that the heavier products are the most affected by this slowing down.

On another side, reactions interfering with mere hydrogenations cannot be avoided and all the more so as the temperature increases. Among the possible interfering processes, hydrogenolysis deserves a special consideration as either a primary process (involving the adspecies themselves) or a secondary one (involving the released products possibly submitted to re-adsorption). In previous reports (10, 11) we have proposed that the occurrence of

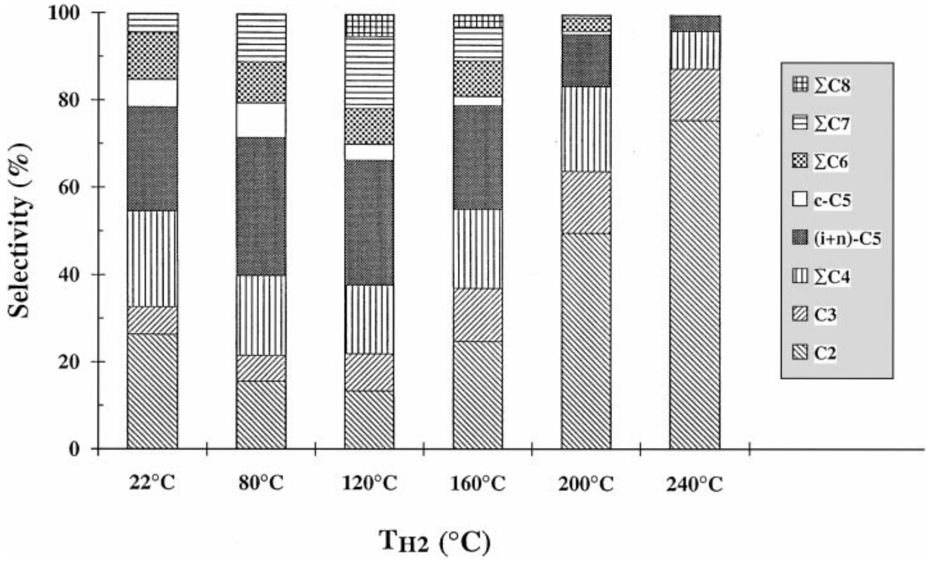

FIG. 8. **Ru**—Distribution of the homologated CH_4 in the C_{2+} products at various T_{H_2}, T_{CH_4} being fixed at 240°C. Data deduced from Fig. 5.

hydrogenolysis is the most reasonable explanation of the decrease of the C_{2+} production beyond some definite temperature. Isomerizations can also be considered as possible interfering reactions and the opposite variations of the *n*- and *c*-C_5 versus T_{H_2} in Fig. 3 probably result from such a process.

These considerations find an immediate application in the case of Ru submitted to given exposures followed by hydrogenations at different T_{H_2} (Figs. 5, 6, 8). In a given set of experiments related to the same T_{CH_4}, the overlayer submitted to hydrogenation keeps the same composition from one experiment to another. The increase of the total C_{2+} production, as well as that of each product, (Fig. 5) and the favoring of the heavier products (Fig. 8) when T_{H_2} is lowered from 240°C are obvious consequences of the slowing down of the hydrogenolysis reactions. However, when the value given to T_{H_2} is below some optimum level, lying between ca 120 and 180°C according to the product considered, it is the slowing down of the hydrogenation-desorption processes which may be considered as responsible for the lowering of the formation of this product and, eventually, of the total C_{2+} production.

The situation is more intricate as regards Pt because just the lowering of the total C_{2+} production was observed when T_{H_2} was diminished below T_{CH_4} (Figs. 3 and 4). Pt is known to be much less active than Ru in hydrogenolysis reactions, which we have checked with our samples (10, 11). Nevertheless, cooling of the Pt sample below 300°C should have caused fast decrease of hydrogenolysis rates. At first sight, an improvement of the total homologation alike that obtained on Ru in similar experiments should have resulted, which was not at all the case. A new way of considering the part played by hydrogenolysis in our two-step sequence must therefore now be introduced.

A number of observations prompt us to think that each exposure of platinum to CH_4 can result in the formation of adspecies heavier, possibly much heavier, than the hydrocarbons released during the subsequent hydrogenation. This can be due to cross-linking between neighbor adspecies or to the growth of adsorbed polyaromatics. The important point as regards the present discussion is that we have to consider that part of the adspecies cannot be removed as such from the surface because they are too heavy. In this case, despite being just the reverse of what we are trying to do, some moderate hydrogenolysis may become a prerequisite to retrieving pieces of too heavy precursors.

In line with these considerations it is worth remarking that:

(i) the C_2–C_4 alkanes formed during *isothermal* experiments (Fig. 1) display re-increases versus temperature above 300°C, necessarily resulting from the breaking of heavier adspecies;

(ii) as can be seen in Fig. 3 related to a set of *dual-temperature* experiments, more octanes are removed from the surface thanks to the lowering of T_{H_2} under 300°C necessarily because they so better escape hydrogenolysis, whereas the reverse holds for the lighter products, including hexanes and heptanes; the increases of the latter products versus T_{H_2} can therefore be reasonably ascribed to the hydrogenolysis of heavier precursors such as octanes;

(iii) despite the decrease of the selectivity to the C_{5+} products when T_{H_2} increases (Fig. 7), the total *weight* of the latter products increases with T_{H_2}, which shows that a large part of them is so retrieved even if a still larger part of them undergoes C–C breaking.

If $T_{H_2} < 100°C$, as on Ru, a significant fraction of the higher adspecies cannot be retrieved during the hydrogenation, whence their decreasing productions, as can be seen from Figs. 3 and 4.

The differences between Pt and Ru behaviors, which have just been commented, clearly appear through the strikingly different aspects of Figs. 4 and 6 which allow one to compare the results of isothermal experiments with those involving hydrogenation at $T_{H_2} < T_{CH_4}$. In the case of Pt (Fig. 4), all the global C_{2+} productions corresponding to a given T_{CH_4} are lower than those of the corresponding isothermal experiment even if an increased selectivity to the heavier products could result from hydrogenations occurring at a diminished temperature. In the case of Ru (Fig. 6), dual-temperature experiments could always entail increased total productions and improved formations of heavier products.

Now, two other points deserve to be remarked. Both of them underline the differences existing between the contribution by Koerts and van Santen and ours.

First, in their contribution the preceding authors reported that hydrogenation of the adspecies at r.t. instead of ≈100°C resulted in the release of ethane and traces of propane (5). The situation is quite different in the present case. On both metals, as we have mentioned above, less products were released at r.t. than at higher temperatures. However, they contained significant proportions of higher alkanes. Examples of that are afforded by the ruthenium which, after having been exposed to CH_4 at 160 or 240°C, allowed about 66% of the converted methane (1.73 or 0.6 μmol, respectively) to be present as C_4–C_6 or C_4–C_7 alkanes, respectively, in the C_{2+} products of the r.t. hydrogenation. The corresponding percentage on platinum was only 8.6% following an exposure at 220°C but amounted to as much as 80% after an exposure carried out at 300°C (respective total C_{2+} productions: 1.07 or 1.29 μmol).

Second, Koerts *et al.* also reported that there exists an optimum total carbon coverage of the metal surface in order to reach an optimum conversion to higher alkanes. That may have been the result of exposures to CH_4 carried out under conditions highly favoring the formation of “bad” carbon (high temperature, low pressure of CH_4). This may also have resulted from the intricacies of the system, which can be illustrated thanks to Fig. 6 related to Ru, a catalyst used in the two studies. The carbon coverage resulting from the exposure at 240°C was necessarily larger than that corresponding to an exposure at 160°C. It is clear that the statement put forward by Koerts *et al.* was obeyed if the subsequent hydrogenations were carried out at 100°C. However, just the reverse was true if the corresponding hydrogenations were carried out at 120°C and still more at 140°C. It thus appears that a systematic and detailed study of the different and numerous factors controlling the system behavior is needed before one can reach definite conclusions.

CONCLUSION

Useful information concerning mechanistic features of the two-step reaction sequence involved in our contribution was furnished by the detailed study of the changes caused by the lowering of T_{H_2} as compared to T_{CH_4}. It is to be noted that the exposure to methane was never performed above 320°C.

Two notions, namely competition of hydrogenolysis with hydrogenation/desorption of the adspecies at high temperatures, on the one hand, and increasing difficulty to desorb the hydrocarbons at low temperatures of hydrogenation, on the other hand, are enough to account for the main features of the ruthenium behavior. This explains, indeed, why the total amount of homologated methane, as well as the selectivity to the higher products (the *n*-pentane above all), can grow when the hydrogenation proceeds at a diminished temperature. One more notion is necessary in the case of platinum, namely the possible formation of adspecies sufficiently heavy for not being efficiently removed by H_2 and, accordingly, requiring some preliminary partial hydrogenolysis for allowing H_2 to dislodge the resulting pieces. This additional assumption allows one to explain why on Pt, contrary to the case of Ru, the total amount of homologated methane resulting from a given exposure to CH_4 was an increasing function of the temperature of hydrogenation, whereas increasing amounts of C_5 to C_7 products were also obtained, despite a diminished selectivity to them.

REFERENCES

1. Belgued, M., Paréja, P., Amariglio, A., and Amariglio, H., *Nature* **352**, 789 (1991).
2. Koerts, T., and van Santen, R. A., *J. Chem. Soc., Chem. Commun.*, 1281 (1991).
3. Belgued, M., Amariglio, H., Paréja, P., Amariglio, A., and Saint-Just, J., *Catal. Today* **13**, 437 (1992).
4. Solymosi, F., Erdöhelyi, A., and Cserényi, J., *Catal. Lett.* **16**, 399 (1992).
5. Koerts, T., Deelen, M. J. A. G., and van Santen, R. A., *J. Catal.* **138**, 101 (1992).
6. 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. Petrol. Chem., San Francisco, CA **37**, 324, 1992]
7. Lenz-Solomun, P., Wu, M. C., and Goodman, D. W., *Catal. Lett.* **25**, 75 (1994).
8. Solymosi, F., and Cserényi, J., *Catal. Lett.* **34**, 343 (1995).
9. Belgued, M., Amariglio, A., Paréja, P., and Amariglio, H., *J. Catal.* **159**, 441 (1996).
10. Belgued, M., Amariglio, A., Paréja, P., and Amariglio, H., *J. Catal.* **159**, 449 (1996).
11. Belgued, M., Amariglio, A., Lefort, L., Paréja, P., and Amariglio, H., *J. Catal.* **161**, 282 (1996).
12. Guczi, L., Sarma, K. V., and Borkó, L., *Catal. Lett.* **39**, 43 (1996).
13. Carstens, J. N., and Bell, A.T., *J. Catal.* **161**, 423 (1996).
14. Amariglio, H., Saint-Just, J., and Amariglio, A., *Fuel Process. Technol.* **42**, 291 (1995).
15. Amariglio, H., Paréja, P., and Amariglio, A., *Catal. Today* **25**, 113 (1995).
16. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18**, 221 (1985).
17. Geus, J. W., and Wells, P. B., *Appl. Catal.* **18**, 231 (1985).
18. Frennet, A., and Wells, P. B., *Appl. Catal.* **18**, 243 (1985).
19. Wells, P. B., *Appl. Catal.* **18**, 259 (1985).