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Oxygen-Free Conversion of Methane to Higher Alkanes through an Isothermal Two-Step Reaction on Ruthenium

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Ruthenium dispersed on silica is able to chemisorb CH_4 at temperatures significantly lower than EUROPT-1 (see the previous articles). At the temperatures used ($\geq$80°C), H_2 desorption parallels CH_4 chemisorption but no C_2H_6 is observed. During the following temperature programmed desorption under flowing argon, CH_4 is removed through a wide range of temperature (from room temperature to 300°C) with a first contribution peaking at less than 100°C. Very small amounts of CH_4 are desorbed after an adsorption carried out at $T \geq 180$°C, due to strong dehydrogenation of the adspecies. Subsequent temperature programmed surface reaction of the remaining adspecies with hydrogen displays upto four CH_4 peaks at well defined temperatures (ranging from ≈ 60 to ≈ 340°C), accompanied by a negligible formation of ethane. No C_γ was formed. The total amount of adsorbed CH_4 and the average H/C ratio of the corresponding adspecies can be derived from these experiments. In a separate set of experiments, CH_4 is switched to H_2 at the end of the exposure step, the temperature being fixed. An immediate formation of alkanes ranging from C_1 to C_6 is then evidenced. A sizeable fraction of the chemisorbed layer can so be homologated to higher alkanes. The influences of the various operating factors are reported. In particular a neat maximum of the C_{2+} production versus temperature (at 160°C) is evidenced and is clearly due to the adverse hydrogenolysis reactions, efficiently catalyzed by Ru. All the results can be interpreted in complete similarity with the Pt case.

INTRODUCTION

In the present article we report the results of a study similar to that of our preceding contributions (1, 2) but relative to the case of Ru instead of Pt. We have chosen Ru because, in addition to being a noble metal, it is also an efficient FT (Fischer–Tropsch) catalyst.

EXPERIMENTAL

1. *Catalyst*

The catalyst was prepared by impregnation of a Spherosil sample (Interchim XOB075 silica, 100 m^2 g^{-1}) with an $RuCl_3$ aqueous solution to incipient wetness. After drying, reduction was carried out in the reactor fed with a flow of H_2 (50 cm^3 min^{-1}), while the temperature was slowly ramped (1 K min^{-1}) to 500°C and maintained constant for 24 h. Between two successive experiments, the catalyst was submitted to a flow of H_2 (50 cm^3 min^{-1}) at 400°C for 2 h in order to remove any carbonaceous residue. It was then fed with a flow of Ar or He (50 cm^3 min^{-1}) to remove H_2 and finally cooled in Ar (or He) at the temperature desired for the experiment. The metal loading of the catalyst (4.7 ± 0.1 wt%) was obtained from the Laboratoire Central d'Analyse (CNRS) by plasma atomic emission spectroscopy.

All the following experiments were carried out on a sample of 100 mg.

2. *Apparatus and Procedures*

The experimental setup and the procedures are exactly the same as previously described (1).

RESULTS

1. *Catalyst Characterization*

1.1. Dispersion evaluation. Dispersion of the catalyst could be determined by measurement of the quantities of (i) H_2, (ii) O_2, or (iii) CO, which the catalyst was able to chemisorb at room temperature (rt). To this end the chemisorption was effected by feeding the catalyst with a flow of the concerned species in the following conditions:

(i) pure H_2 at ordinary pressure, 50 cm^3 min^{-1}, 15 min;
(ii) Ar at ordinary pressure loaded with 100 ppm O_2 until no more O_2 consumption could be detected with an O_2 trace analyzer (Engelhard Mark II electrochemical meter);
(iii) pure CO at ordinary pressure, 50 cm^3 min^{-1}, 1 min.

The amount of H_2 chemisorbed was deduced from the spectrum of TPD (temperature programmed desorption) which resulted from feeding the catalyst with an Ar flow (50 cm^3 min^{-1}) while the temperature was ramped at 8 K min^{-1} (Fig. 1). The corresponding amount of CO was attained through the temperature programmed surface

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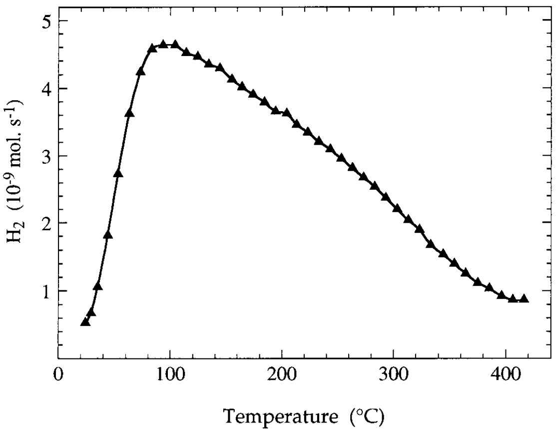

FIG. 1. TPD spectrum of H_2 preadsorbed on 100 mg of 4.7 wt% Ru/SiO_2. Adsorption: H_2 (1 bar, 50 cm^3 min^{-1}, 15 min, rt). TPD (8 K min^{-1}) under Ar (1 bar, 50 cm^3 min^{-1}).

reaction (TPSR) of the CO monolayer with H_2 (50 cm^3 min^{-1}, 8 K min^{-1}). Figure 2 shows the resulting CH_4 peak.

Assuming H/Ru_S and O/Ru_S ratios equal to 1 we could so estimate that the surface Ru atoms of the sample amounted to 17.0 and 17.8 μmol, respectively. The adsorbed CO was converted to 16.0 μmol of CH_4, which may be considered in good agreement with the preceding results if one considers that some CO molecules can occupy two metal sites (bridged adsorption). On the basis of 17 μmol of surface Ru atoms, the dispersion of our catalyst can be estimated as equal to ca. 36%.

1.2. Electron microscopy examination. A sample, intended to be submitted to electron microscopy examination, was prepared as previously described. After reduction, it was fed with a flow of Ar in order to remove the H_2 and cooled to rt. O_2 was then chemisorbed on the Ru particles by feeding them with a flow of (Ar + 100 ppm O_2). The sample could then be removed from the reactor without suffering any damage. It was lightly ground in a small mortar and subsequently dispersed in alcohol by ultrasonic treatment. A drop of the suspension so obtained was deposited on a copper grid covered with carbon. The samples were examined with a Philips CM20 high-resolution transmission microscope equipped with a microprobe system (EDAX microanalysis). Magnifications ranging from 88,000 × to 380,000 × were used with the microscope operated at 200 kV. Subsequent enlargements could be obtained by using thin photographic paper.

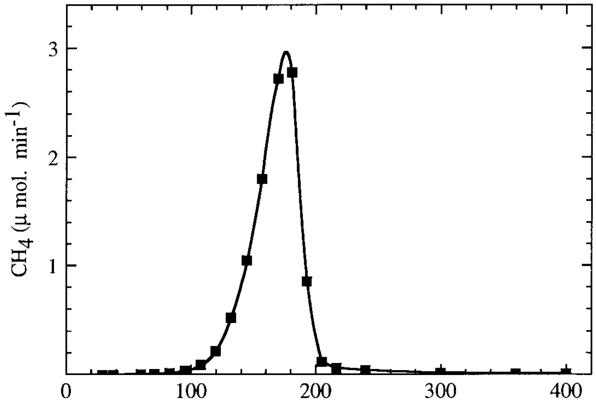

FIG. 2. H_2-TPSR of CO preadsorbed on 100 mg of Ru/SiO_2. Adsorption: CO (1 bar, 50 cm^3 min^{-1}, 1 min, rt). TPSR (8 K min^{-1}) with H_2 (1 bar, 50 cm^3 min^{-1}).

Figure 3a presents a typical representation of the observations repeated on numerous parts of the sample. Most of the particles display linear dimensions between 15 and 80 Å, which is quite consistent with the dispersion previously determined.

We have also observed a sample which had been used in numerous experiments, consisting in chemisorption of CH_4 effected under various conditions and followed either by TPD and TPSR with H_2 or by hydrogenation at the same temperature. After this set of experiments, the catalyst had been submitted to H_2 at 400°C for 1 h, fed with a flow of Ar in order to remove H_2, and passivated like the fresh sample specially prepared for the electron microscopy observation. Figure 3b presents a typical view of the observations which do not differ from that on the fresh sample.

2. *Evolution of H_2 during Exposure to CH_4*

When Ru was exposed to flowing CH_4 at various fixed temperatures, T_{CH_4}, release of H_2 was evidenced from $T_{CH_4} \geq 80°C$. At $T_{CH_4} \leq 100°C$ the rate of H_2 evolution displayed a clear maximum versus time on stream but, at higher temperatures, only monotonic decreases were observed (Fig. 4). Figures 5 and 6 show how the amount of H_2 released during 5-min exposures to CH_4 increased as a function of T_{CH_4} and of the flow rate, respectively. Contrary to the case of Pt, there was no C_2H_6 formed during exposure to CH_4 at any temperature.

3. *Amount of Adsorbed Methane and Its Variation with Operating Factors*

In order to determine the amount of adsorbed methane at the end of the exposure step, we carried out a TPD interrupted at 300°C and followed by a TPSR of the remaining adspecies with H_2.

3.1. TPD spectra. After exposure to CH_4 under given conditions of temperature, duration, and flow rate, the Ru sample was cooled to rt as quickly as possible (1 min or so) while being kept in static CH_4. The reactor was then purged with flowing He and the temperature was linearly ramped up to 300°C. Only CH_4 was formed during heating. Figure 7 collects TPD spectra corresponding to various temperatures of exposure ranging between 80 and 200°C,

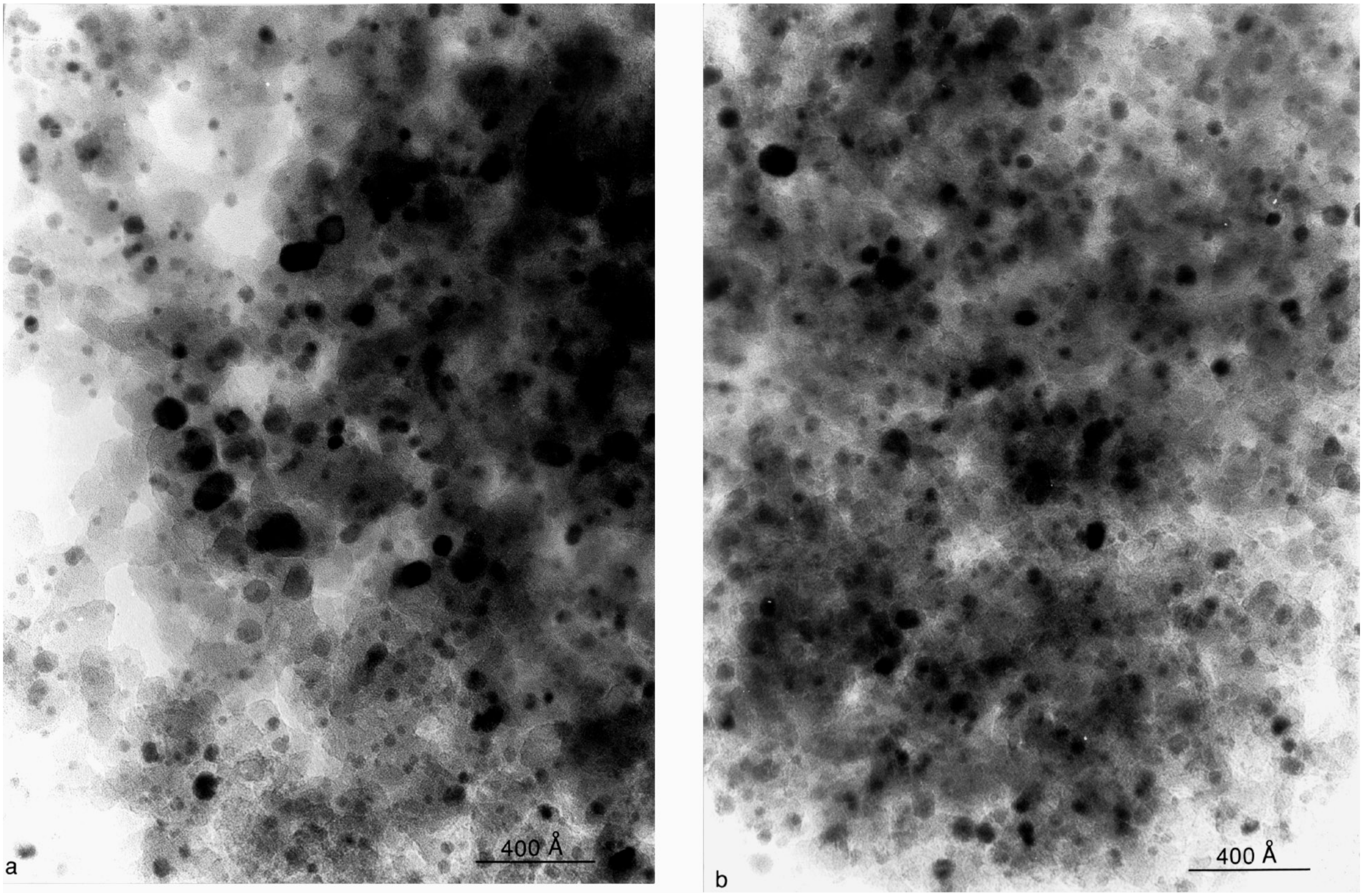

FIG. 3. Electron micrographs of the catalyst; (a) fresh, (b) used.

other operating conditions being fixed. They display a low temperature peak (at $T < 100^\circ C$), followed by more or less distinguishable peaks and a progressive extinction of the CH_4 desorption at about 300°C. The dominant feature of these spectra is the very strong decrease of the CH_4 evolved throughout the entire range of TPD when the preliminary chemisorption of CH_4 was carried out at temperatures above 160°C.

No H_2 and no hydrocarbon other than CH_4 were evidenced during the TPD's.

3.2. TPSR Spectra. Cooling the catalyst to rt at the end of each TPD and exposing it to H_2 immediately resulted in a CH_4 production with a small amount of ethane and propane production. All these productions reached negligible levels beyond a few minutes. Thereafter, the temperature was ramped up to ca. 450°C, which caused the removal of CH_4 accompanied by only traces of C_2H_6. Figure 8 collects the TPSR spectra related to CH_4 which were obtained after the corresponding TPD spectra of Fig. 7. When CH_4 was chemisorbed at $T_{CH_4} \leq 160^\circ C$, mainly two peaks appeared (at 70 and 140°C). For $T_{CH_4} > 160^\circ C$, two other CH_4 peaks appeared at ≈ 230 and $\approx 320^\circ C$, which made the total amount of CH_4 produced during the TPSR much higher than the corresponding one obtained after any exposure at $T_{CH_4} \leq 160^\circ C$.

3.3. Variation in the amount of CH_4 adsorbed versus temperature. The quantities of CH_4 evolved during the different steps previously described as well as that of C_2H_6 released during the TPSR with H_2 can be found in Table 1. The corresponding amount of CH_4 chemisorbed in each case is easily derived and its variation with temperature is represented in Fig. 5 where we have already plotted the variations with temperature of the amount of H_2 evolved during the exposure to CH_4. The parallelism between these two curves is obvious. Moreover, their comparison shows that the carbonaceous species left on the surface after the exposure to CH_4 are deeply dehydrogenated.

3.4. Influence of the duration of the exposure to CH_4. In order to illustrate the influence of the duration of the exposure to the flow of CH_4, only one set of other operating conditions was chosen. The choice of 160°C as temperature of exposure resulted from the fact that the production of higher alkanes by hydrogenation of the chemisorbed species was the largest at that temperature (see Section

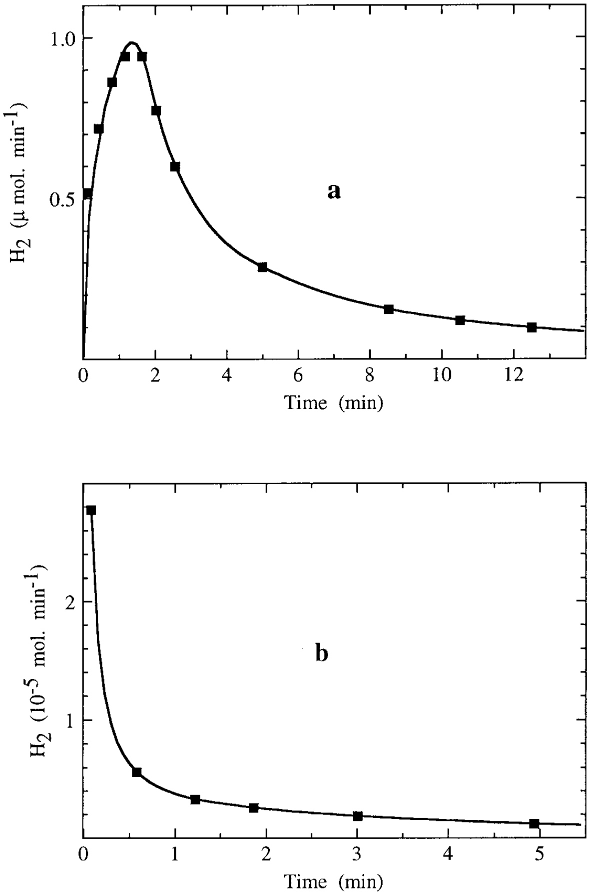

FIG. 4. Molar flow rates of H_2 evolved at 80°C (a) or 160°C (b) during exposure of Ru to CH_4 as a function of time on stream. Conditions: 100 mg of Ru/SiO_2 exposed to 375 cm^3 min^{-1} of CH_4.

4.1). Every exposure was followed by the same succession of experiments as in the previous cases. Figures 9 and 10 collect the corresponding TPD and TPSR spectra and Fig. 11 gives the variation of the amount of CH_4 adsorbed versus the duration of exposure.

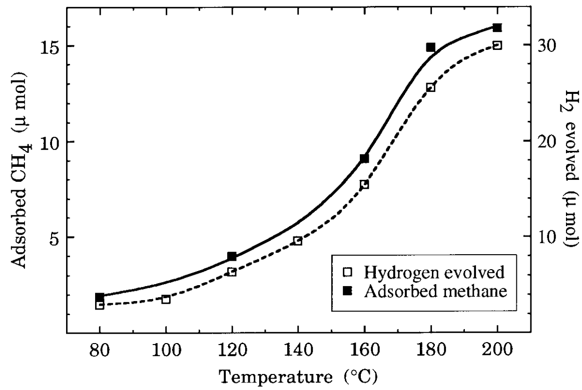

FIG. 5. Molar amounts of H_2 evolved and of CH_4 adsorbed during 5-min exposures of Ru to CH_4 as a function of temperature. Conditions: 100 mg of Ru/SiO_2 exposed to 375 cm^3 min^{-1} of CH_4.

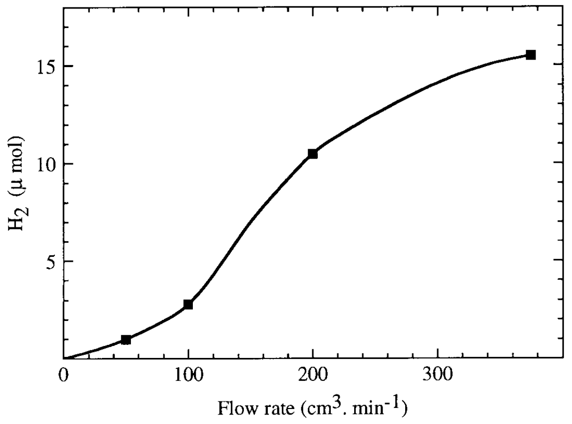

FIG. 6. Molar amounts of H_2 evolved during 5-min exposures to CH_4 at 160°C as a function of the flow rate of CH_4. Same catalyst sample as for Figs. 4 and 5.

4. *Formation of Higher Alkanes by Hydrogenation of the Surface Species*

At the end of the preliminary exposure of Ru to CH_4, when CH_4 was switched to H_2, significant amounts of higher alkanes ranging up to C_6 (and traces of C_7) were immediately released, as in the case of Pt. The total production and its distribution depended upon the same factors as for Pt, i.e., temperature and duration of the exposure to CH_4, flow rate and pressure of CH_4, and pressure of H_2 during the second step. Ethane was always the most abundant product even if, under certain conditions, most of the CH_4 was converted into pentanes. No cyclo-alkanes (or only traces) were formed and that was different from what happened on platinum. At least in the upper part of the temperature range explored, the alkanes were rapidly formed upon admission of H_2 since most of the production was obtained in 10 s at 160°C. Only this fast production is here taken into account and, accordingly, attention has been paid only to

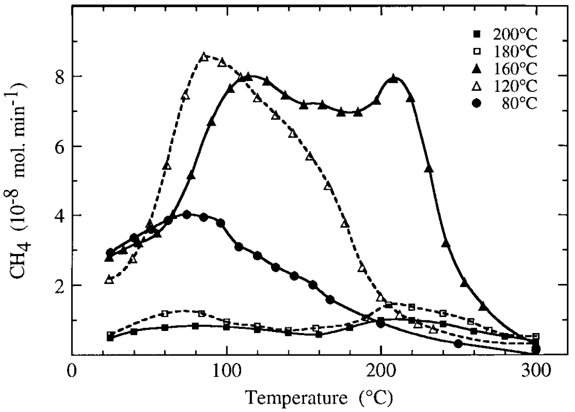

FIG. 7. TPD spectra following exposures of Ru to CH_4 at various temperatures. Conditions: Exposures as for Fig. 5; flow rate of He, 200 cm^3 min^{-1}; ramp of temperature, 8 K min^{-1}.

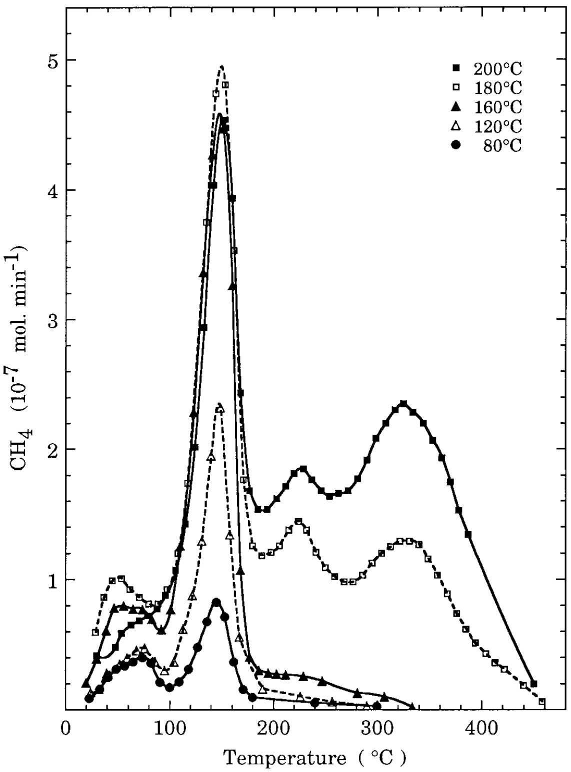

FIG. 8. Profiles of H_2-TPSR of the adspecies remaining on the Ru surface after the TPD corresponding to Fig. 7. Conditions: flow rate of H_2, 50 cm^3 min^{-1}; ramp of temperature, 6 K min^{-1}.

this total production without any attempt at rate measurements.

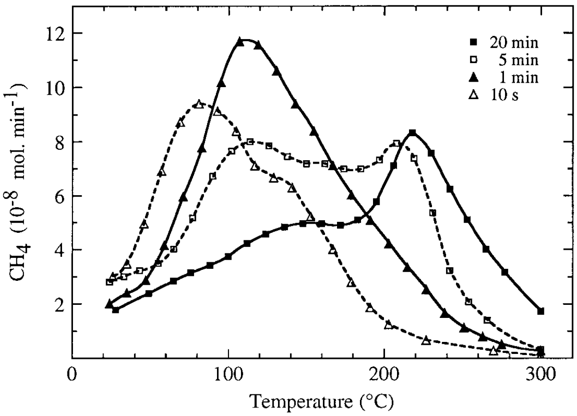

FIG. 9. TPD spectra following exposures of Ru to CH_4 at 160°C for different durations. Other conditions as for Fig. 5.

4.1. Influence of the temperature. Figure 12 shows the variation of the molar quantities of each product versus temperature, every other operating condition being fixed. The overall C_{2+} production is also shown and is clearly seen to be at a maximum at 160°C. However, the temperature causing the maximum of the heavier alkanes (C_{4+}) was slightly lower (140°C instead of 160°C, except for *i*-C_4). The fractions of homologated CH_4 which were converted to each of the C_{2+} products can be seen in Fig. 13.

For a number of experiments, the quantities of CH_4 chemisorbed during the exposure step were determined in a separate set of experiments. To this end, after

TABLE 1

Variation of the Total Amounts of the Methane Adsorbed and of the Products Collected during TPD and H_2-TPSR, as a Function of Temperature

Temperature	CH_4				
(°C)	[a]	[b]	[c]	C_2H_6[d]	$CH_{4\,ads}$
80	0.65	0.66	0.60	0.00	1.91
120	1.25	0.60	2.15	0.00	4.00
160	1.80	1.90	4.80	0.31	9.12
180	0.35	3.60	10.20	0.38	14.9
200	0.25	3.10	11.60	0.48	15.9

Note. The amounts are expressed in μmol. Conditions of the chemisorption of CH_4: 1 atm, 375 cm^3 min^{-1}, 5 min.

[a] Amount of methane collected during the TPD.

[b] Amount of methane collected in the flow of H_2 at rt.

[c] Amount of methane collected during the H_2-TPSR.

[d] Amount of ethane collected during the H_2-TPSR.

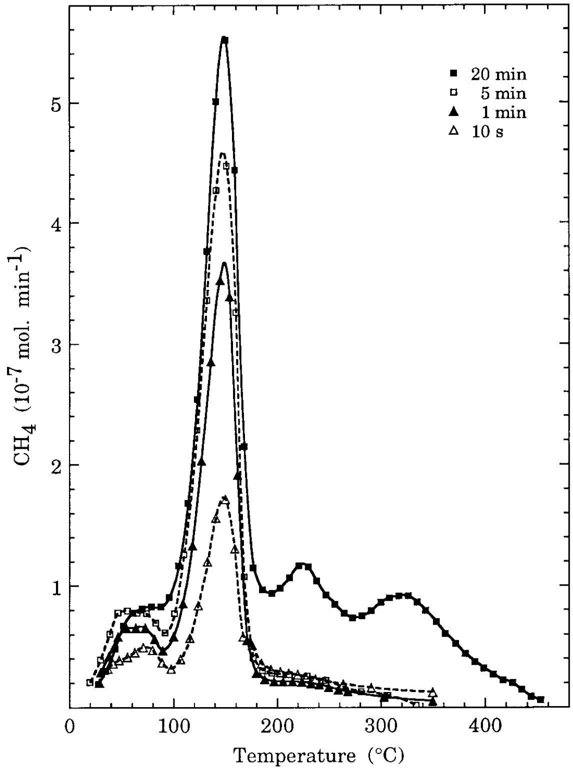

FIG. 10. Profiles of H_2-TPSR of the adspecies remaining on the Ru surface after the TPD corresponding to Fig. 9. Conditions of the TPSR as for Fig. 8.

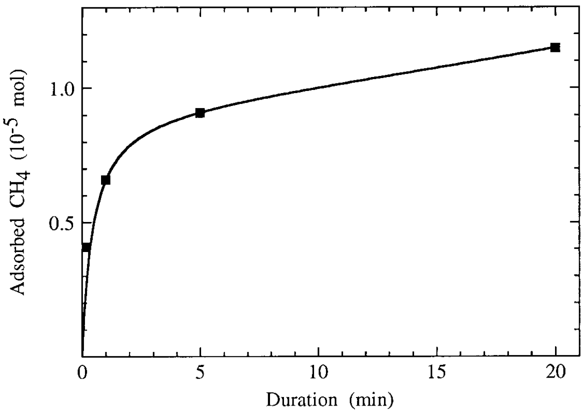

FIG. 11. Molar amounts of CH_4 adsorbed at 160°C as a function of the exposure duration. Data are deduced from Figs. 9 and 10.

having been exposed to CH_4, the catalyst was cooled to rt. The amount of chemisorbed CH_4 was determined from subsequent TPD and H_2-TPSR, as explained in (1). The fraction of *chemisorbed* methane which was homologated could so be determined. The result is given in Fig. 14.

4.2. Influence of the duration of exposure. The effect of the duration of CH_4 exposure was examined at 160°C and is illustrated in Fig. 15. Unlike the case of Pt, all the products were formed in increasing amounts when the exposure was prolonged. However, the increase was much stronger for the heavier than for the lighter alkanes. In this respect it can be seen that the overall production increased from 3.36 to 4.08 μmol when the exposure was lengthened from 5 to 20 min, whereas the amount of hexanes was multiplied by a factor of three.

Two additional experiments clearly showed how the continuous removal of H_2 during the exposure to CH_4 matters in relation with the subsequent alkane production. After exposure of the Ru to the flow of CH_4 for either 1 or 5 min the reactor was closed and the exposure to *static* CH_4 was prolonged for 4 or 15 min, respectively. The corresponding subsequent productions equaled those obtained after 1 or 5-min exposures. Further *useful* chemisorption of CH_4 did not take place during CH_4 exposure under static conditions. There was no evidence for a modification of the previously adsorbed species either. That observation strongly underlines that *the removal of H_2 by flowing CH_4 is a requirement for obtaining adspecies in a state allowing their mutual bonding.*

4.3. Influence of the flow rate of CH_4. The preceding comment is exemplified by the results presented in Fig. 16 showing how the total production and how the production of each family of alkanes varied versus the flow rate of CH_4, every other operating condition being fixed. If the C_2 production tends to level off when the flow rate is over 300 cm^3 min^{-1}, a continuous increase of the production of the other alkanes can be noticed and the more so as the rank of the alkane is the greater. These results are consistent with those obtained on Pt in similar experiments (2).

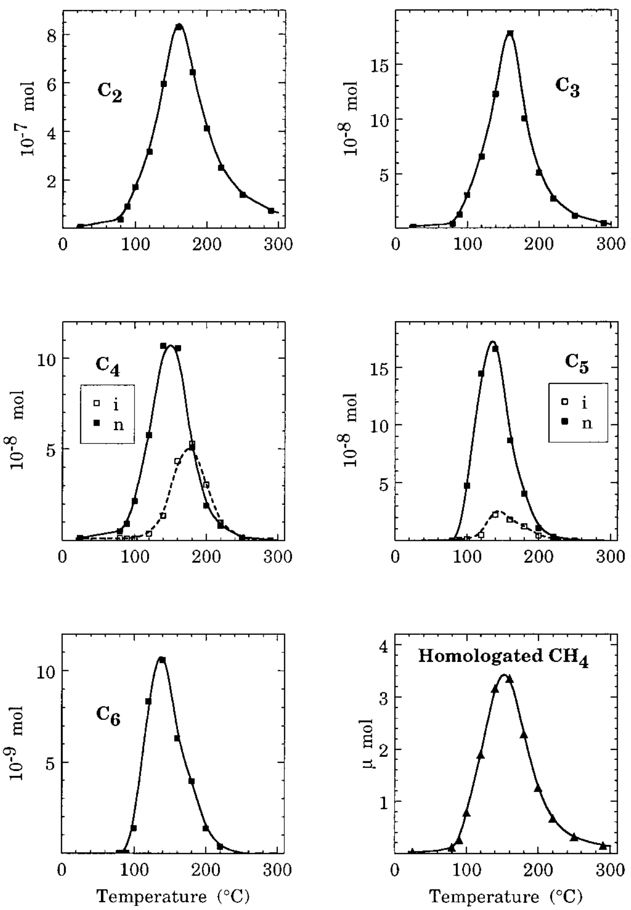

FIG. 12. Molar amounts of the total homologated methane and of the various C_{2+} products resulting from exposures of Ru to methane at various temperatures (step 1) and subsequent hydrogenations at the same temperature (step 2). Conditions: 100 mg of Ru/SiO_2. Step 1: exposure to CH_4 (1 bar, 375 cm^3 min^{-1}, 5 min); Step 2: exposure to H_2 (1 bar, 50 cm^3 min^{-1}).

4.4. Repetition of uninterrupted CH_4/H_2 cycles. Ten successive isothermal CH_4/H_2 cycles were applied to the Ru sample. Each of them comprised a 5-min exposure to CH_4 (375 cm^3 min^{-1}) at 160°C and a 1-min exposure to H_2 (50 cm^3 min^{-1}) at the same temperature. No decrease of the total C_{2+} production per cycle was evidenced.

4.5. Reproducibility of the results. Two kinds of reproducibility may be distinguished, according to the scale of time. The numerous experiments which were necessary to obtain such results as those given in Figs. 12 or 15 took several days and their uncertainty did not exceed a few percent. In contrast, long use of the catalyst during several weeks could result in a loss of the total C_{2+} production of a given CH_4/H_2 cycle which could reach up to 25%. In such cases we preferred to replace the used sample by a fresh one, instead of trying to rejuvenate the used sample by a prolonged subjection of H_2 at an elevated temperature.

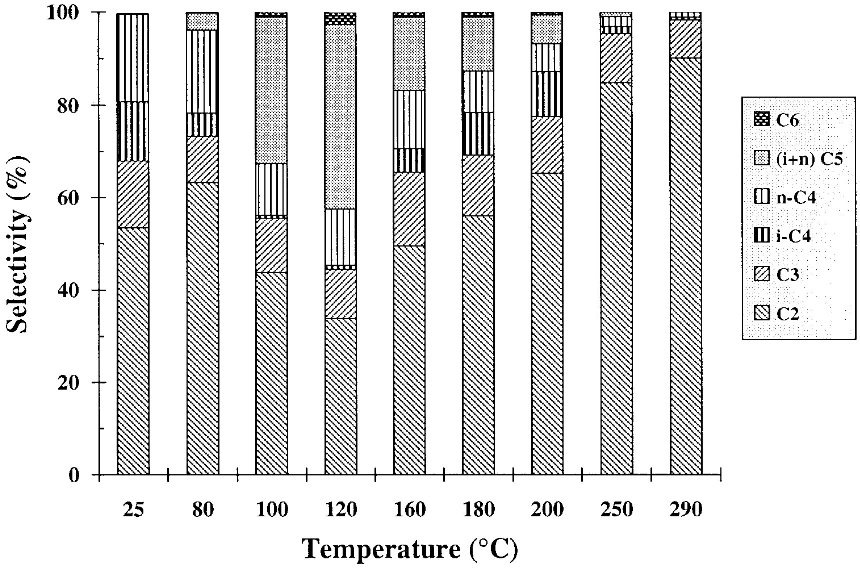

FIG. 13. Distribution of the homologated CH_4 in the C_{2+} products at various temperatures. Data are deduced from Fig. 12.

In case of interruption of the experiments for a period of time exceeding 1 week, a very efficient way of maintaining the catalyst properties was to cover its surface with oxygen chemisorbed under mild conditions, by submitting the catalyst at rt to a flow of He loaded with 1‰ O_2. Removal of the oxygen with H_2 at 300°C allowed us to recover the catalyst in a state which was always the same as that prevailing before this passivation.

4.6. Evidence for the hydrogenolysis activity of the catalyst. The decrease of the C_{2+} production beyond 160°C, with other operating conditions being fixed (Fig. 12), can be explained by the interference of the homologation process with the hydrogenolysis of the alkane surface precursors. Hydrogenolysis activity of Ru was tested versus temperature by using a mixture purchased from Air Liquide and consisting of C_3, *n*- and *i*-C_4, *n*- and *i*-C_5, and *n*-C_6 diluted in H_2. The concentrations of alkanes in this mixture (C_3, 2360 ppm; *i*-C_4, 1940 ppm; *n*-C_4, 2060 ppm; *i*-C_5, 1980 ppm; *n*-C_5, 1970 ppm; *n*-C_6, 240 ppm) were similar to those found in the reaction products. At each temperature, the hydrogenolysis products were analyzed after a 5-min feed of the catalyst by this mixture flowing at 50 cm^3 min^{-1}.

Consumption of *n*-hexane started at about 100°C and that of *i*- and *n*-pentane at 140°C. The concentrations of propane and butanes first increased up to 140–160°C, as they were formed from pentane and hexane, before sharply decreasing at higher temperatures. Methane and ethane increased from 100 to 120°C and ethane began to decrease from 210°C only. Interference with hydrogenolysis was all the more confirmed as the alkanes submitted to hydrogenolysis in our experiments are already adsorbed on ruthenium when H_2 is admitted.

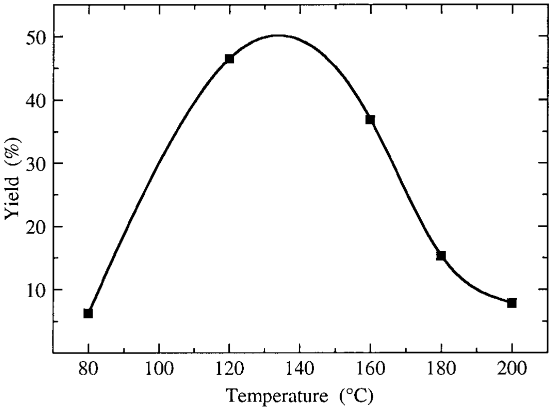

FIG. 14. Yield of conversion of the adsorbed methane as a function of the temperature. Data are deduced from Figs. 5 and 12.

DISCUSSION

1. *Methane Chemisorption*

As in the case of Pt (1), evolution of H_2 parallels the chemisorption of CH_4 on Ru but, in contrast with this previous case, no formation of C_2H_6 is observed. However, it must be noted that no H_2 desorption from Pt could be measured under our conditions below 150°C, whereas Fig. 4 shows that H_2 desorption accompanying CH_4 adsorption on Ru could easily be monitored from as low a temperature as 80°C. Therefore CH_4 chemisorption and H_2 removal occur faster on Ru than on Pt, so that H-deficient adspecies can build up on the surface at lower temperatures. Such a situation must favor C–C bonding rather than ethane desorption. Except for the desorption of ethane, the

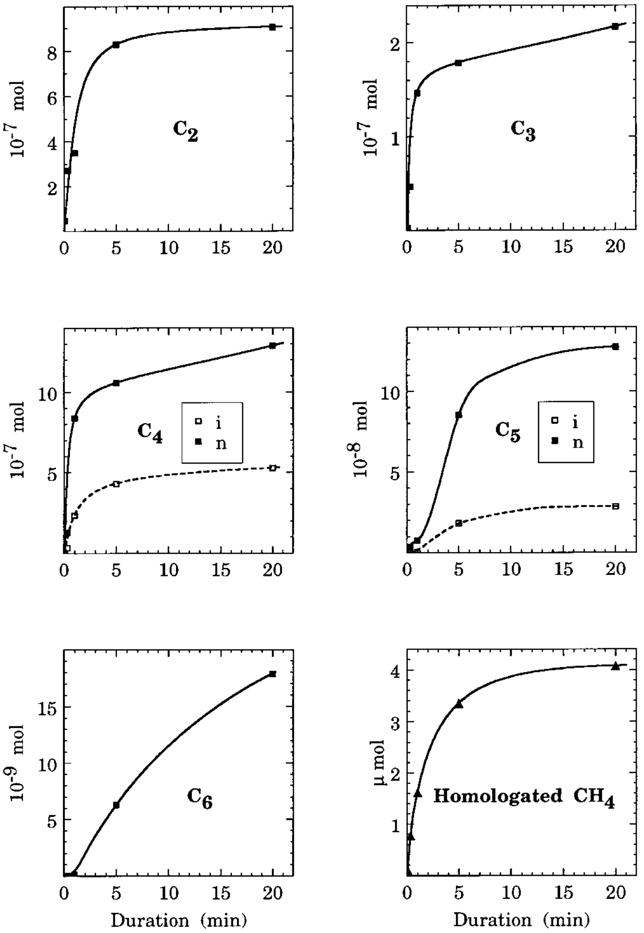

FIG. 15. Variation with the duration of the exposure to methane of the molar amounts of the total homologated methane and of the various C_{2+} products resulting from exposures of the Ru catalyst to CH_4 at 160°C and subsequent hydrogenations at 160°C. Other conditions as for Fig. 12.

same elementary processes as on Pt can be imagined to take place on Ru, although to likely different extents for a given set of operating conditions.

As in the case of Pt (1), approximate averages of the H/C ratio of the CH_x adspecies can be evaluated in two ways giving rise to x_1 and x_2 (using the same symbols and considerations as in the preceding case). Here we recall only that x_1 and x_2 are limiting values of x and are such as

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

and

$$x \leq x_2 = 4\frac{Q_{\mathrm{CH_4\,TPD}}}{Q_{\mathrm{CH_4\,ads}}},$$

where

$Q_{\mathrm{CH_4\,ads}}$ is the molar quantity of C_1 units adsorbed at the end of the first step,

Q_{HS} means the molar amount of superficial hydrogen, assumed to be essentially bonded to C,

$Q_{\mathrm{H_2\,des}}$ and $Q_{\mathrm{C_2H_6\,des}}$ are, respectively, the total amounts of H_2 and of C_2H_6 desorbed during the first step,

$Q_{\mathrm{CH_4\,TPD}}$ represents the total amount of CH_4 removed during the TPD.

The results corresponding to exposures either of equal durations but carried out at different temperatures or carried out at a constant temperature but of increasing durations are presented in Tables 2 and 3. The same comments as for Pt can also be made here. x_2 (more reliable than x_1) shows that most of the exposures to CH_4 gave rise to highly (although not completely) dehydrogenated adspecies.

2. *TPD and TPSR Spectra*

Tendencies very similar to those exhibited by the TPDs carried out on Pt (1) are also present in the TPD spectra of Fig. 7 but at much lower temperatures of exposure to

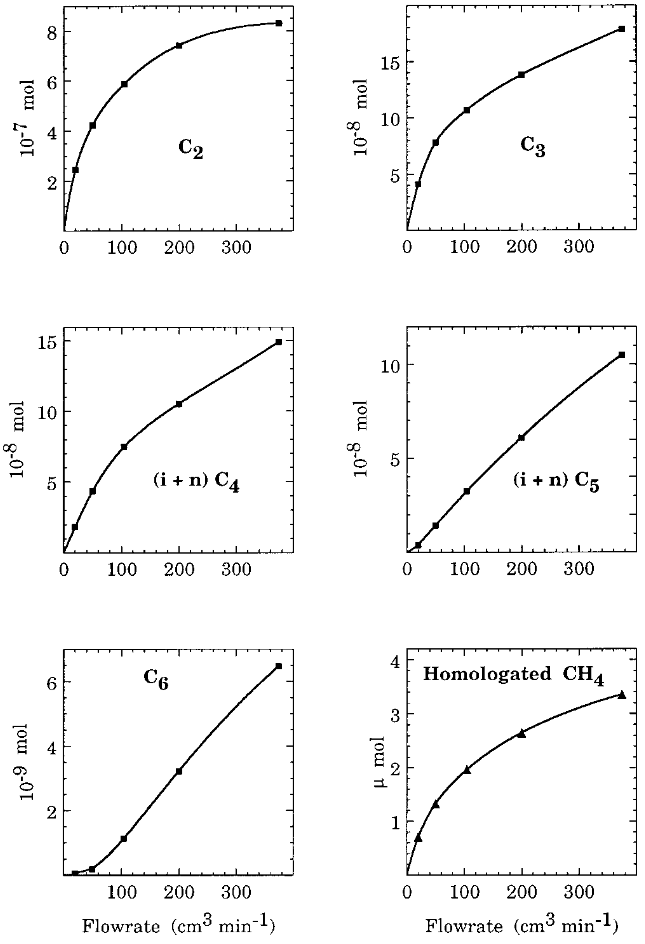

FIG. 16. Variation with the flow rate of CH_4 of the molar amounts of the total homologated methane and of the various C_{2+} products resulting from exposures of the Ru catalyst to CH_4 at 160°C and subsequent hydrogenations at 160°C. Other conditions as for Fig. 12.

TABLE 2

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

T (°C)	$Q_{H_2\ des}$ (μmol)	$Q_{CH_4\ TPD}$ (μmol)	$Q_{CH_4\ ads}$ (μmol)	x_1	x_2
80	3.00	0.65	1.90	0.84	1.36
120	6.40	1.25	4.10	0.87	1.22
160	15.5	1.80	9.10	0.59	0.79
180	25.6	0.35	14.9	0.56	0.09
200	30.0	0.25	15.9	0.22	0.06

Note. Conditions: 5-min exposures; 375 $cm^3\ min^{-1}$; 1 atm.

CH_4 than in the case of Pt. These spectra mainly consist of two contributions, the first one interpretable as resulting from the associative desorption of C_1 and H adspecies (low temperature peak) and the second one resulting from the progressive decomposition of heavier adspecies leading to departure of some CH_4 into the gaseous phase. Undistinguishable from that first contribution when the exposure is effected at a low temperature (80°C), the second contribution strengthens greatly for an exposure at 120°C and even more for an exposure at 160°C. Above these temperatures (for $T_{CH_4} = 180$°C and $T_{CH_4} = 200$°C), only very small quantities of CH_4 can be removed throughout the entire range of the following TPD. These results are striking in light of the fact that the total amount of CH_4 adsorbed on the surface continued to increase with adsorption temperature (cf. Section 3.3 and Fig. 5). However the adsorbed CH_x species are more depleted in H_2 as adsorption temperature increases (see in Fig. 5 the curve related to H_2 evolved during the exposure), so that there is insufficient hydrogen to allow CH_4 to be formed from its possibly different precursors. In case of Pt, adsorption had to be carried out at more than 300°C to lead to a similar observation, although to a lesser extent (1). The lesser dehydrogenation undergone by the adspecies on Pt, as compared with that on Ru, can also be viewed through the larger amount of CH_4 involved in the second TPD peak on Pt, as compared to the corresponding one on Ru. This agrees with our interpretation of the CH_4 released at high temperature as being due to the decomposition of C_{2+} chemisorbed precursors. Similar comments can be done regarding Fig. 9. Even a 10-s exposure at 160°C allows a sizeable amount of CH_4 to be chemisorbed but mainly light and relatively little dehydrogenated adspecies are formed. Longer exposures result in a strongly increased evolution of CH_4 in the high temperature part of the TPD, whereas the reverse tendency is shown in the low temperature one.

TABLE 3

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

Duration	$Q_{H_2\ des}$ (μmol)	$Q_{CH_4\ TPD}$ (μmol)	$Q_{CH_4\ ads}$ (μmol)	x_1	x_2
10 s	1.80	1.50	4.10	3.12	1.46
1 min	7.10	1.75	6.60	2.15	1.06
5 min	15.5	1.80	9.10	0.59	0.79
20 min	18.9	1.63	11.5	0.71	0.56

Note. Conditions: Exposures carried out at 160°C; 375 $cm^3\ min^{-1}$; 1 atm.

Severely H-deficient adspecies are expected to be present on the Ru surface at the end of each TPD. Their subsequent subjection to H_2, after recooling of the sample, causes immediate formation of CH_4 and that is not surprising in view of what is already known concerning the reactivity of fresh carbon deposits with H_2 (3). This low temperature production of CH_4 after TPD is not observed in the case of Pt (1), most probably because no pure carbon deposits are formed on this metal even during TPD. Unlike on Pt also, CH_4 is the only product of the following TPSR (except for traces of ethane) and up to four clearly distinct peaks of CH_4 can be exhibited by the spectra. Only two peaks are present when the preliminary exposure to CH_4 is effected at a temperature too low to allow a sufficient amount of chemisorbed species to build up on the surface. A striking difference between the TPD and TPSR spectra concerns the changes exhibited by them as a function of the conditions of exposure to CH_4. Whereas the TPD spectra undergo modifications in the position and extent of their different parts, the positions of the different peaks of which the TPSR spectra are made remain quite constant, whereas their heights are liable to vary. Such was also the case on Pt not only for the methane peak but also for the ethane and propane peaks which are absent here. That behavior strongly suggests that only a small number of well defined carbonaceous adspecies are present on the surface at the end of the TPD and that the quantity of each of them depends upon the conditions of the preliminary exposure to CH_4. The first TPSR peak can reasonably be interpreted as due to the removal of the C_1 adspecies remaining after hydrogenation at rt. We suggest that the other peaks originate in the hydrogenation and/or in the hydrogenolysis of the aforementioned carbonaceous adspecies.

Remarkably, no C_γ was formed in our experiments (no reincrease of CH_4 formation beyond 400°C), despite the heating to which the adsorbed species were subjected during TPD. That is in sharp contrast to what was observed when Ru and Co were made to react with CH_4 at much higher temperatures (4).

3. *Thermodynamic and Mechanistic Considerations*

What has already been stated concerning the *thermodynamic analysis* of the whole process (2) obviously also holds in the present case. Chemisorption of CH_4 with parallel release of H_2 at a low partial pressure, C–C bonding between neighboring H-deficient C_1 adspecies, removal of the C_{2+} surface precursors by H_2 at a pressure higher than that at which it was released during the first step, and the necessary corresponding expenditure of energy remain the key notions explaining why CH_4 can be homologated on adequate metal surfaces in reductive conditions by the use of an isothermal two-step reaction sequence.

Concerning the *mechanistic considerations*, little new has to be added here to our reports on Pt (1, 2) except for the fact, already mentioned, that adsorption of CH_4—and the resulting C–C bonding—can take place at much lower temperatures on Ru (2) than on Pt. As Ru is a very efficient catalyst of hydrocarbon hydrogenolysis (5), it is not surprising that the maximum of homologation ability versus temperature be observed sooner than on Pt. It is this ability of the metal to catalyze the C–C bond scissioning by H_2 which also allows one to understand the variation of the product distribution versus temperature (see Fig. 13). For example, we can see that the contribution of C_2 decreases when T_{CH_4} increases from 80 to 120°C, due to increasing coverages making C–C bonds more easily formed, whereas its contribution reincreases for $T_{CH_4} > 120°C$. The reverse is of course true for C_5 which turns out to be the most favored homologated product at 120°C. In contrast with what was observed on Pt, no cyclo-pentane or cyclo-hexane is formed on Ru, which likely results from a worse fitting of their precursors to the surface geometry and to the interatomic distances of Ru, as compared to Pt. Worse fitting may result in lesser amount of concerned precursors and/or in their easier hydrogenolysis during the second step.

The results shown in Figs. 12 and 14 lead to the following remarks:

(i) Although the methane produced during hydrogenation escapes *direct* measurement since it cannot be distinguished from the CH_4 already present in the reactor at the onset of the second step, we can state that a great part of the CH_4 chemisorbed in the first step reverts to CH_4 during the second step or remains on the surface, involved in C_nH_y adspecies which react with H_2 only at higher temperatures (see the H_2-TPSR spectra).

(ii) The lowering of the heavier alkanes at $T < 120°C$ is not solely due to the lowering of the surface coverage since the conversion of the chemisorbed species is also decreasing. Increased average distances between adspecies and, still more, insufficient dehydrogenation have also to be invoked to explain this feature.

(iii) The lowering of the total C_{2+} production above 160°C as well as that of the selectivity to the heavier alkanes above 140°C have another origin since the quantity of chemisorbed CH_4 goes on increasing with the temperature of exposure. Hydrogenolysis is the most reasonable explanation of that and we have put the stress on the occurrence of hydrogenolysis in Section 4.6.

An interesting feature of the product distribution, which might also have been commented in the case of Pt, is the neat increased selectivity to the heavier alkanes, resulting from increases of either the duration of exposure or the flow rate of CH_4, in such conditions that the total amount of adsorbed methane does not much increase. For instance one can see that when the duration of exposure to CH_4 increases from 5 to 20 min at 160°C, the quantity of CH_4 chemisorbed increases by no more than 25% (Fig. 11), whereas that of the C_6 produced is approximately multiplied by a factor of 3 (Fig. 15). Two effects of exposure lengthening can explain the results. The first one is obvious since more adspecies build up on the surface, which leads to an increased probability of C–C bonding. The second effect lies in the fact that H_2 is only progressively removed from the adspecies by the flowing CH_4, so that the prolonging of the exposure does not only cause increased adsorption but also it allows the initially adsorbed species to lose more H_2 and so increases their ability to give rise to C–C bonding. Moreover, additional sites become available for increased adsorption of CH_4.

CONCLUSION

The main results of this contribution constitute mere extensions to the case of Ru of those obtained with Pt. Possible CH_4 adsorption at lower temperatures, no release of C_2H_6 during adsorption of CH_4, lower H/C ratios of the resulting adspecies, and stronger contribution of hydrogenolysis during the hydrogenation step are the main differences displayed by Ru. The reason that the thermodynamic barrier of CH_4 homologation can be overcome still obviously lies in the amount of energy which has to be supplied to the H_2 released at a low partial pressure during the first step in order to compress it and make it usable in the second step.

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