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# Periodic operation of a catalyst as a means of overcoming a thermodynamic constraint. The case of methane homologation on metals

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**Abstract**

Periodic operation of a catalyst can be a way of overcoming a thermodynamic constraint. Homologation of methane is thermodynamically disfavored. However, a two-step procedure using metal catalysts under non-oxidative conditions allows the thermodynamic limitations to be circumvented. Metal catalysts, such as Pt, Co and Ru are exposed first to methane and then to hydrogen. In their *dual-temperature procedure*, van Santen et al. carry out the first step with dilute methane at a high temperature (usually 725 K), which allows the endothermic decomposition of methane to take place. Part of the C deposits may yield higher alkanes up to $C_4$–$C_5$ through the following hydrogenation at a much lower temperature (368 K). In contrast, we carry out these two steps at atmospheric pressure and *at the same but moderate temperature* (usually less than 570 K). In this case, chemisorption of methane is accompanied by release of hydrogen whereas coupling of H-deficient $CH_x$ adspecies may take place. Numerous higher alkanes up to $C_7$–$C_8$ are then removed by supplying hydrogen at ordinary pressure and at the same temperature as that of the first step. The driving force can be found in the energy which has to be supplied in order to compress part of the dilute hydrogen removed in the first step to make it usable in the second one. The influence of some key factors is studied.

## 1. Introduction

Improvements in rates or selectivities of reaction can sometimes result from the cyclic rather than the steady feeding of a catalyst (see other contributions in the present issue).

In reviewing some results recently reported in the field of methane up-grading into higher hydrocarbons, we propose to show that a cyclic procedure may be used to overcome *thermodynamic* (rather than just kinetic) limitations that make a steady state process impossible.

The simplest methane homologation that leads to the formation of ethane, namely:

$$2\,CH_4 \rightarrow C_2H_6 + H_2$$

displays a highly positive $\Delta G^\circ$ ( +70.5 kJ at 500 K) and can therefore proceed only at very low conversions. In addition, it is well known that its reverse reaction, frequently used as a catalytic test reaction, has practically no thermodynamic limitation. This is why oxidative coupling of methane, discovered some ten years ago [1], has become the route most explored for directly homologating methane (mainly to $C_2$'s) [for reviews see [2–5]]. In oxidative coupling, the driving force consists of the negative $\Delta G^\circ$ contribution of the $H_2$ oxidation process to water, whereas a significant part of methane is wasted as carbon dioxide.

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However, two recent independent contributions have shown that a cyclic process could be used to homologate $CH_4$ in the absence of oxygen [6–13]. Similar observations [14] were also reported soon after the foregoing ones. These studies make use of supported metallic catalysts alternately fed with $CH_4$ or $H_2$ but in one of them the methane contacts the catalyst at a rather elevated temperature followed by cooling prior to hydrogenation [7,9,11] whereas in the second one [6,8,10,12,13] the whole cycle can proceed isothermally at a moderate temperature. We will now examine these two procedures in turn.

## 2. Homologation resulting from carbon deposition at high temperatures

The basic idea underlying the experiments reported by Koerts and van Santen [7] is that some particular surface carbon species, possibly a carbide, formed by contacting metals with $CH_4$ at a rather high temperature, can then react with $H_2$ to form alkanes. However one cannot find a unique temperature at which the intermediate carbon species could form and be subsequently hydrogenated to an alkane other than just $CH_4$. It follows that the two steps must proceed at different temperatures. In the first step, the methane has to decompose on the metal, a process that occurs easily at a high temperature, whereas the subsequent

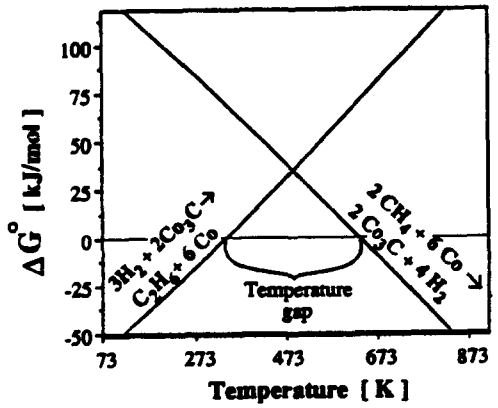


Fig. 1. Gibbs free energy as a function of the temperature for the decomposition of methane on cobalt and the hydrogenation of cobalt carbide to ethane [9].

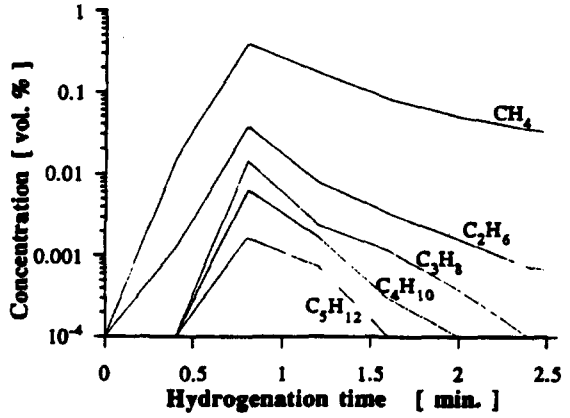


Fig. 2. Hydrogenation of surface carbon created from methane decomposition at 723 K, on a 10 wt.-% cobalt catalyst as a function of the hydrogenation time. For butane and pentane, the sum of the iso-and n-products is shown [9].

hydrogenation must proceed at a much lower one. This principle is represented in Fig. 1 and the temperature gap can be considered as a *thermodynamic constraint.*

Several transition metals, among which Co and Ru are the most effective, allow alkanes up to $C_5$ to be obtained upon application of this procedure. $CH_4$ decomposition occurs in the first step when the catalyst sample is fed with $CH_4$ diluted in helium. Typically a pulse of 3 min of (He, 0.5% $CH_4$) (45 ml/min) was used at 723 K. The catalyst was then cooled in 100 s below 470 K to avoid aging of the carbon species and hydrogenation proceeded at about 370 K in a $H_2$ flow of 22.4 ml/min at ambient pressure.

Fig. 2 shows the way in which the alkanes are released during hydrogenation on Co as a function of time on stream, while Fig. 3 gives the selectivity to the main products ($C_1$–$C_4$) as a function of the hydrogenation temperature on Ru (a) and Co (b). This figure also gives the quantity of C hydrogenated and accordingly underlines the fact that not all the deposited carbon could be removed during the second step.

After decomposition of $CH_4$ on the catalyst, three forms of deposited carbon were evidenced on the surface through three $CH_4$ peaks observed upon TPSR (temperature-programmed surface reaction) with $H_2$. These three peaks correspond to carbon species already discovered and named

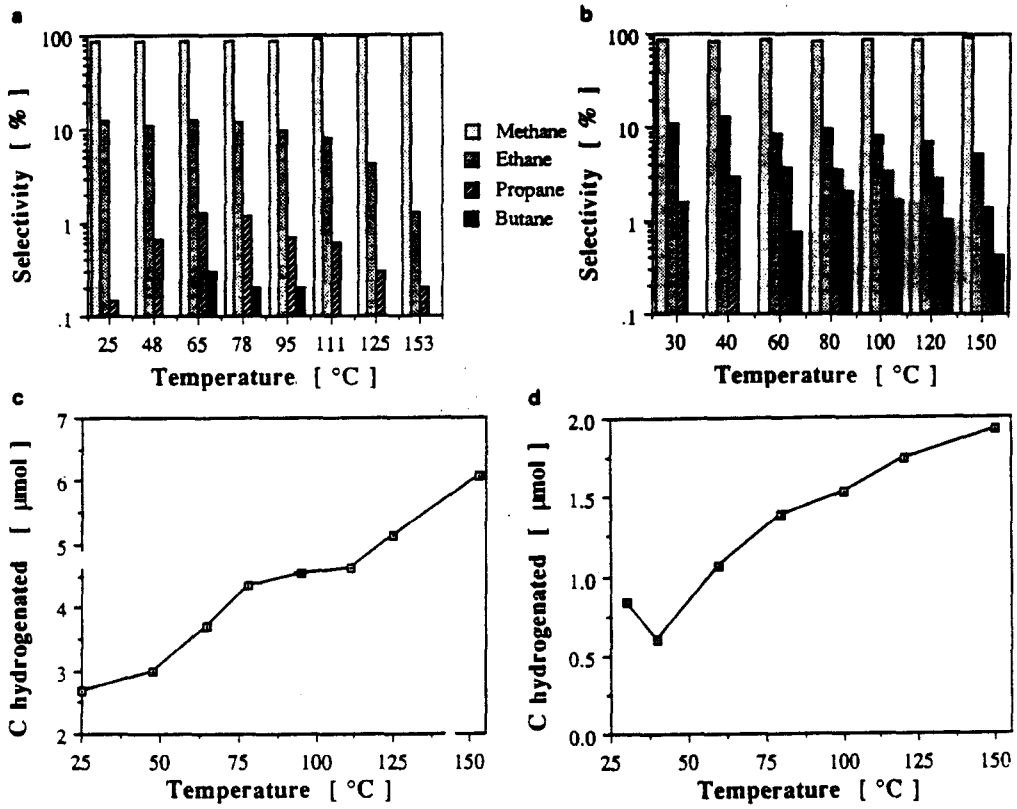


Fig. 3. Product distributions as a function of the hydrogenation temperature of surface carbon species deposited from methane at 723 K: (a) 5% $Ru/SiO_2$. (b) 10% $Co/SiO_2$. Total amount of surface carbon that is hydrogenated: (c) Ru; (d) Co [9].

$C_\alpha$, $C_\beta$ and $C_\gamma$ by McCarty and Wise [15] for C that results from CO disproportionation (Boudouard reaction). It is well known that $C_\alpha$ is a carbidic type of carbon and is able to react at room temperature. $C_\alpha$ was considered by Koerts and van Santen to be responsible for the formation of the $C_{2+}$ alkanes, according to the same mechanism as that often cited for the Fischer–Tropsch synthesis. $C_\beta$ is a less reactive surface carbon species hydrogenated mainly into $CH_4$ between 370 and 670 K. $C_\beta$ is thought to be an amorphous phase where C–H bonds are still present. $C_\alpha$ can readily be transformed into $C_\beta$ whereas the reverse is only partially possible. Finally $C_\gamma$ is assumed to be graphitic carbon, hydrogenatable only between 670 and 870 K. As there is a progressive conversion of $C_\alpha$ into $C_\beta$ and eventually into $C_\gamma$, there is an optimum coverage (ca. 20%) of the surface with C in order to maximize the $C_{2+}$ production.

The optimum overall yield for the formation of $C_{2+}$ hydrocarbons (13%) was obtained on a $Ru/SiO_2$ catalyst at a surface coverage of 0.18. A pulse of (He, 0.28% $CH_4$) (4.57 µmol of $CH_4$) was given to 300 mg of a Ru catalyst. The resulting deposit consisted of 2.66 µmol $C_\alpha$, 1.61 µmol $C_\beta$ and 0.04 µmol $C_\gamma$. Upon subsequent hydrogenation at 368 K, 2.66 µmol of surface carbon reacted, of which 21% was incorporated into $C_{2+}$ alkanes. However about half of the C deposit was not reacted with $H_2$, so that fast contamination of the surface with carbon can be expected if repeated cycles are applied.

## 3. Homologation resulting from methane chemisorption at moderate temperatures

Our own view of $CH_4$/metal chemistry, although different, also led to $CH_4/H_2$ cycles *but at lower temperatures*. Both steps could be carried out either at the same temperature [6,8,10,12,13] or the second could be done at a much lower tem-

perature [8,10]. It has long been known that methane can simply chemisorb on transition metal surfaces at temperatures much lower than those required for its decomposition. This property explains the ability of several metals to catalyze exchange reactions between $CH_4$ and $D_2$ at such moderate temperatures [for a review see [16]]. As at least one C–H bond must be broken upon chemisorption, $H_2$ desorption can be expected to parallel the chemisorption process and is indeed observed when the temperature is high enough. If the removal of $H_2$ is sufficiently prolonged, H-deficient $CH_x$ species ($x < 3$) appear on the surface and C–C bond formation between neighboring $CH_x$ species can be expected. The formation of ethane, observed when platinum is exposed to a flow of methane [6], can be interpreted according to this view but the amount of

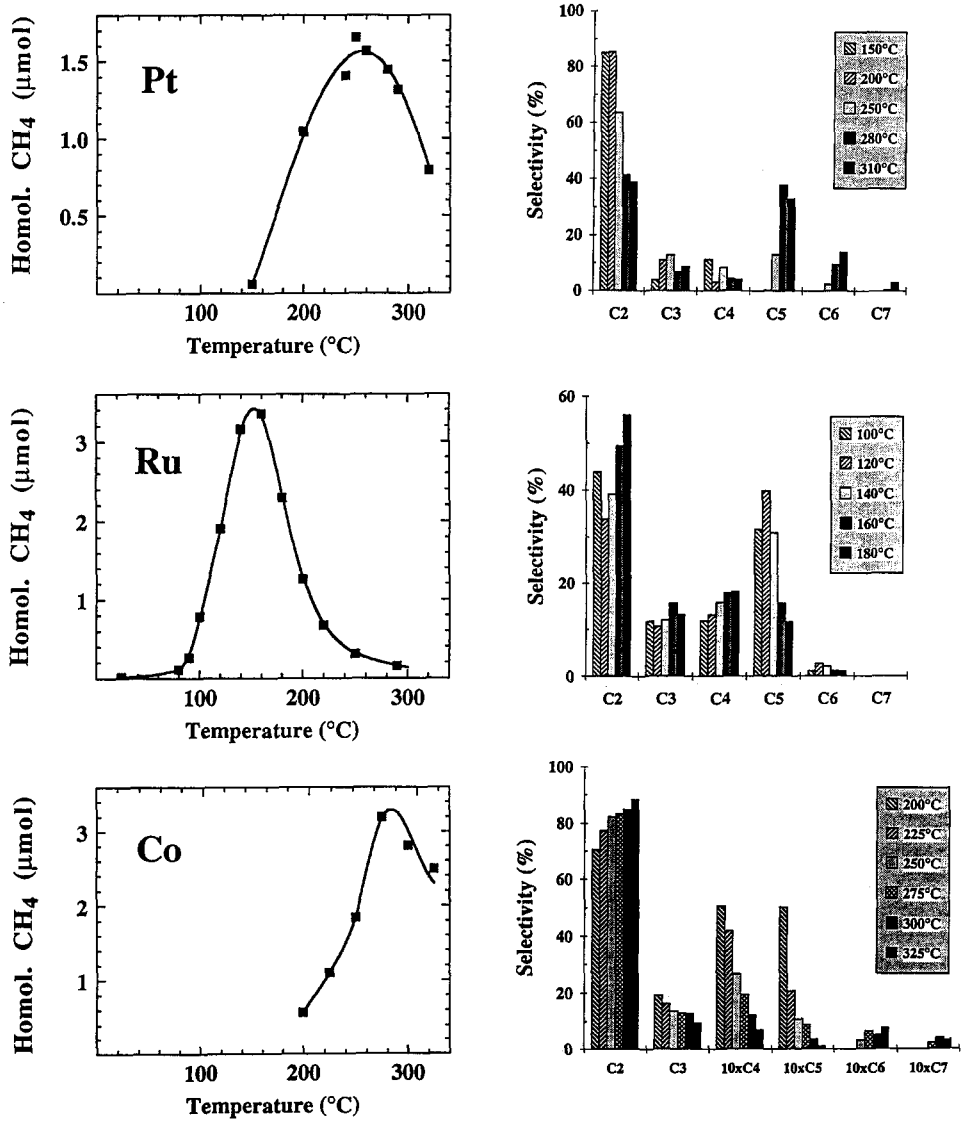


Fig. 4. Molar amounts of the total homologated methane and selectivities to the $C_2+$ products resulting from exposures of Pt, Ru and Co catalysts to methane at various temperatures (step 1) and subsequent hydrogenations at the same temperature (step 2) [8]. Conditions: Pt — 100 mg of EUROPT-1 (6.3 wt.-% Pt); step 1: exposure to $CH_4$ (0.1 MPa, 400 ml $min^{-1}$, 1 min); step 2: exposure to $H_2$ (0.1 MPa, 50 ml $min^{-1}$). Ru —100 mg of 4.7 wt.-% $Ru/SiO_2$; step 1: exposure to $CH_4$ (0.1 MPa, 375 ml $min^{-1}$, 5 min); step 2: exposure to $H_2$ (0.1 MPa, 50 ml $min^{-1}$). Co —600 mg of 2 wt.-% Co/kieselguhr; step 1: exposure to $CH_4$ (0.1 MPa, 250 ml $min^{-1}$, 4 min); step 2: exposure to $H_2$ (0.1 MPa, 50 ml $min^{-1}$).

ethane is about one order of magnitude lower than that of $H_2$ and both are produced just briefly. This material balance unambiguously shows that H-deficient carbonaceous species build up on the surface during the chemisorption and that, if $C_{2+}$ precursors are formed, they are too strongly linked to the surface to desorb spontaneously. This is the reason why subsequent exposure to a flow of $H_2$ is necessary, while at the same time serving as an efficient way of releasing numerous alkanes from the surface.

### 3.1. Isothermal experiments

Among a number of transition metals (Ni, Fe, Co, Pd, Pt, Rh, Ru), Pt and Ru appear to be the most efficient ones. Fig. 4–6 report some typical

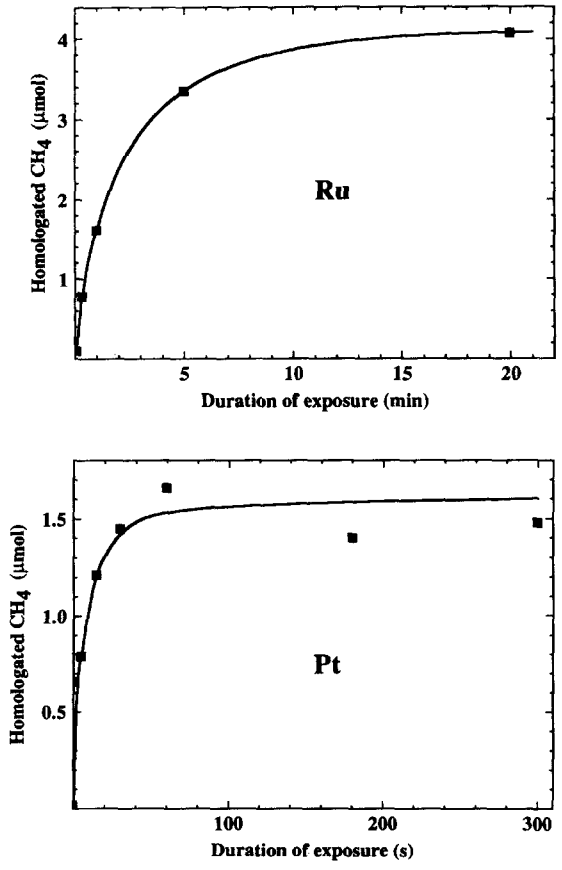


Fig. 5. Molar amounts of the total homologated methane at 523 K on Pt catalyst and at 433 K on Ru catalyst as a function of the duration of exposure to flowing methane [12]. Other conditions are the same as for Fig. 4.

results obtained with Pt, Ru and Co [8]. Prior to exposure to the $CH_4$ flow, the catalysts were cleaned of any C residue in a flow of $H_2$ at 673 K and then of chemisorbed hydrogen in a flow of argon at the same temperature. Cooling to the desired temperature between 370 and 570 K was then effected before switching from argon to methane. Hydrogenation immediately followed the exposure to the flow of methane.

Some significant features have to be stressed concerning the results obtained with Pt and Ru particularly.

Concerning the influence of the *temperature* (Fig. 4), we can first notice that the productions were maximum at 523, 433 and 553 K for Pt, Ru and Co, respectively. The existence of such maxima results from interference with hydrogenolysis of the alkanes produced at rates increasing with temperature. A second remark concerns the distribution of the products which disobeyed the Anderson–Schulz–Flory distribution, even on a qualitative basis in a few cases, since the selectivity to the $C_5$'s was almost as high as that to $C_2$ on Pt at 553 and 583 K and higher than that to $C_2$ on Ru at 393 K. A third important feature is that most of the products were quickly retrieved. In most cases, and especially at temperatures corresponding to the largest $C_{2+}$ productions, only traces of $C_{2+}$ compounds were present in the $H_2$ flow beyond about 10–20 seconds. The lighter n-alkanes (up to $C_5$) were obtained at maximum concentrations during the first seconds of hydrogenation, as could be observed by sampling the gas leaving the reactor just at the beginning of the hydrogenation. The production of ethane in particular was so fast that a small dose (0.2 ml) of the gas leaving the reactor just at the beginning of the hydrogenation could contain a few per cent of $C_2$, a concentration by two orders of magnitude higher than that reported at the maximum of Fig. 2. This concentration was higher by several orders of magnitude than that corresponding to the equilibrium of the homologation reaction at conditions prevailing in the reactor during this transient operation.

An additional remark concerns the fact that *normal* alkanes were not always formed even though they were often the principal products. More than twenty kinds of alkanes could be obtained at the temperature of the maximum yield. For example, equal amounts of branched and normal hexanes were produced with Pt at 523 K, whereas 40% of the pentane was cyclopentane.

Contrary to what was reported in the preceding non-isothermal experiments (Section 2), the amount of homologated products monotonously increased with the *duration of exposure to* $CH_4$ and the increase in surface coverage that resulted. For instance, increasing the duration of exposure of Ru from 5 s to 20 min brought about a 40-fold increase of the $C_{2+}$ amount (Fig. 5). In parallel, the fraction of reacted $CH_4$ converted to $C_2$ decreased from 88 to 44% whereas that converted to $C_{4+}$ alkanes increased from 1.7 to 39.6% [12]. Similar results were obtained with Pt [10] but the production levelled off for shorter exposures than in the case of Ru (ca. 2 min instead of 8–10 min) (Fig. 5). Increasing the exposure duration always resulted in a shift of the alkanes toward the heavier ones.

A noteworthy result concerns the influence of the *flow rate of* $CH_4$ during the first step, as displayed in Fig. 6. Very small amounts of $C_{2+}$ alkanes were obtained when the reactor was closed and the catalyst exposed to *static* $CH_4$. Increasing the flow rate of $CH_4$ resulted in increasing the $C_{2+}$ production and in favouring the heavy alkanes.

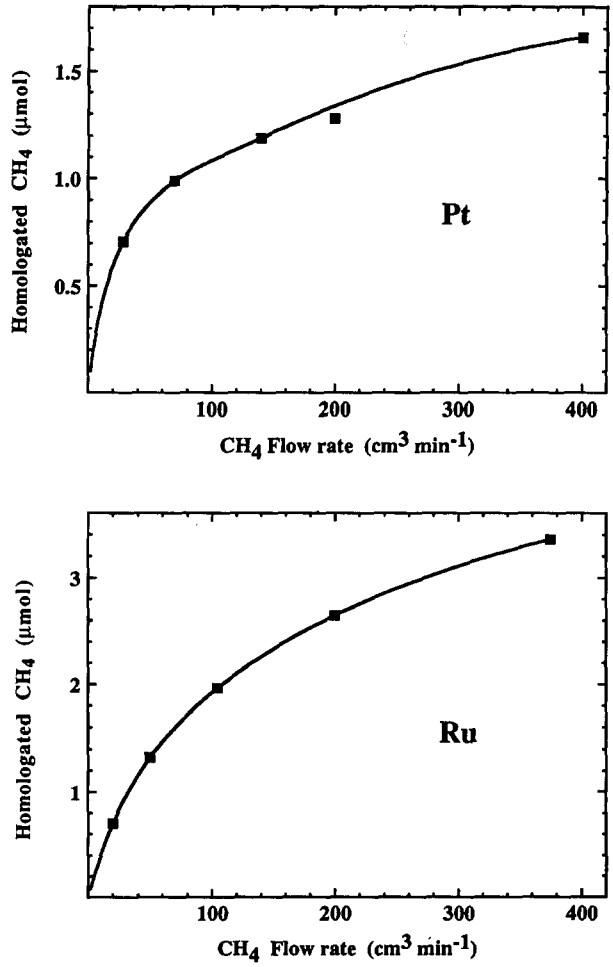


Fig. 6. Molar amounts of the total homologated methane at 523 K on Pt catalyst and at 433 K on Ru catalyst as a function of the flow rate of methane during the exposure step. [12] Other conditions are the same as for Fig. 4.

This is to be paralleled with more efficient removal of hydrogen when the latter is ensured by higher flow rates of $CH_4$.

### 3.2. Dual temperature experiments

In addition to these results, mention must be made of the catalyst behavior in dual temperature experiments. What was researched was the effect of a lowering of the temperature of the second step (after a given $CH_4$ exposure) upon the extent of homologation and the distribution of the products [8,10].

After a given exposure of Ru to $CH_4$ at $T_1 = 433$ K, different values were ascribed to the temperature, $T_2$, of the second step in successive separate experiments. When $T_2$ decreased from 433 to 373 K, the amount of homologated methane increased from 2.61 (maximum isothermal production) to 3.70 μmol (Fig. 7). When $T_2$ was further decreased, the amount of homologated $CH_4$ decreased slowly and at room temperature the same amount as at 433 K was obtained [10]. Still deeper effects of the decrease of the hydrogenation temperature were observed upon the selectivities since the isothermal cycle at 433 K resulted in 54.8% and 11.4% of the homologated methane being respectively converted into $C_2$ and $C_5$ instead of 18.5% and 53.3% in the 433 K/373 K cycle.

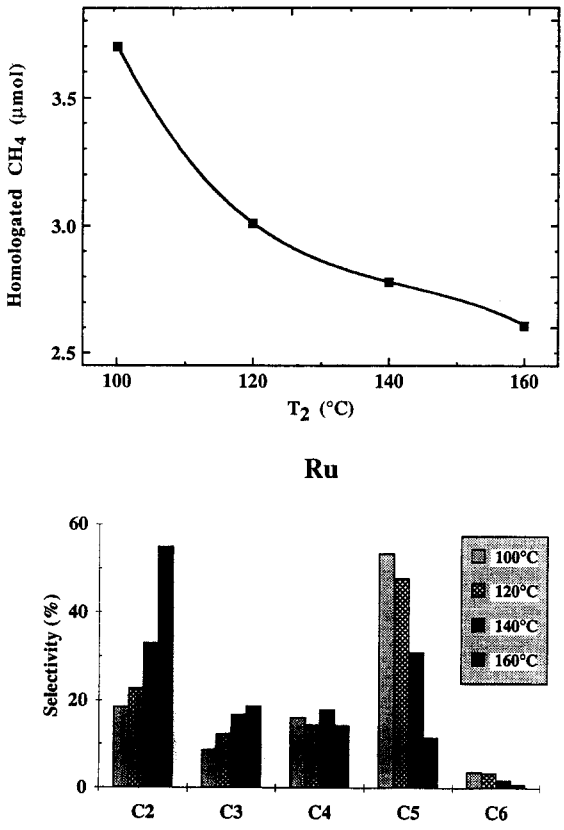


Fig. 7. Dual temperature experiments: variation with hydrogenation temperature ($T_2$) of molar amounts of total homologated methane and of selectivities to $C_2+$ products resulting from exposure of the Ru catalyst to methane at a fixed temperature ($T_1$) and subsequent hydrogenation at $T_2$ ($T_2 < T_1$) [12]. Conditions: 100 mg of 4.7 wt.-% $Ru/SiO_2$; step 1: exposure to $CH_4$ (0.1 MPa, 375 ml $min^{-1}$, 3 min, $T_1 = 433$ K); step 2: exposure to $H_2$ (0.1 MPa, 50 ml $min^{-1}$, $T_2$ variable)

The situation was different on Pt, revealing a *continuous decrease* in the amount of homologated $CH_4$ when the second step was conducted at a lower and lower temperature [10]. For example, 3.50 or 1.45 μmol of homologated $CH_4$ resulted from the same exposure to $CH_4$ at 573 K, depending on whether the subsequent hydrogenation was effected at 573 or at 373 K. However the effect on the selectivity of the lowering of $T_2$ at a constant $T_1$ was qualitatively the same as for Ru. In the preceding example 40.1% $C_2$ against 43.0% $C_5$–$C_8$ resulted from the isothermal cycle instead of 19.8% and 76.2% respectively for the 573 K/373 K cycle.

### 3.3. Yields

In every experiment the amount of adsorbed $CH_4$ could be determined by cooling the catalysts quickly after exposure and carrying out a TPSR with $H_2$. In this way the yield for a given cycle, defined as the fraction of *adsorbed* $CH_4$ that was homologated, could be evaluated; it varied with the nature of the metal and the conditions. On Ru, about 46% of the chemisorbed $CH_4$ could be converted to $C_{2+}$ alkanes in isothermal cycles at 393 K and about 50% on Pt at 523 K. However, because the amount of incoming $CH_4$ during the exposure was higher by several orders of magnitude than that which the metal surface could accommodate at complete coverage, the yield

expressed on the basis of the *incoming methane* was always very small (1‰ in the best cases). A much greater amount of catalyst or a much smaller amount of $CH_4$ should have been used in order to improve the yield substantially. We have recently succeeded in improving the yield by using 1 g of EUROPT-1 in a stirred batch reactor equipped with a hydrogen trap made of supported Pd. Under these conditions only the methane adsorbed was consumed and had to be replaced by an equal quantity of fresh methane to allow the repetition of the experiment. More than 40% of the total $CH_4$ consumed during the first step was converted to $C_{2+}$ alkanes [17].

## 4. Comparison of both procedures

At first glance both procedures seem very similar as both of them require forced feed cycling of the catalysts. They cause methane to form an intermediate product with the metal and to react further with hydrogen to the $C_{2+}$ species. However what is fundamentally different in both procedures is the nature of the intermediate product.

In one of them [7,9,11] the metal is contacted by $CH_4$ at a much higher temperature than that required for its simple chemisorption so that deep decomposition of the $CH_4$ can really take place and bring about carbon deposits or even carbide formation as postulated by the authors. Re-hydrogenation of these species at the same temperature can only lead to $CH_4$ whereas hydrogenation of the most reactive part of them can occur at a much lower temperature and can result in $C_{2+}$ species. In this respect this experiment is very reminiscent of that carried out by Rabo et al. [18] when they submitted the C deposit brought about by the CO disproportionation (at 573 K) to $H_2$ doses at room temperature. In such circumstances even Ni, which ordinarily gives rise only to $CH_4$ in the CO/$H_2$ reaction, led to the formation of $C_1$ to $C_4$ alkanes. In that case the C–C bonds of the $C_2$–$C_4$ alkanes were likely formed during the hydrogenation of the C deposit. Most probably the same occurs here even though the C displays a different origin.

In contrast to the preceding case, when the catalyst is contacted with $CH_4$ at a temperature usually well below 573 K, $CH_x$ species (not merely C) concentrate on the surface with parallel evolution of hydrogen. At a sufficiently high concentration of these species on the surface, when their dehydrogenation is sufficient (although incomplete), C–C bonding can be expected. In this respect, it is worthwhile to notice that in a similar situation created by adsorption of alkanes or alkenes (ethylene for instance) at similar temperatures, most of the C–C bonds are not disrupted [19]. At the end of the first step we can therefore expect the surface to be partly covered with $C_{2+}$ precursors. Positive proof of the existence of such precursors was given by the desorption of several hydrocarbons (particularly olefins) when the Pt sample received a pulse of CO at the end of the exposure to methane and before hydrogenation [20]. This helps us to understand why the TPSR with $H_2$ of the adspecies gives a result different from that observed by van Santen and coworkers [9]. As soon as the catalyst was fed with hydrogen at room temperature, several higher alkanes were produced and the proper TPSR could not be carried out before these alkanes ceased being formed. During the temperature ramp, no evidence of $C_\gamma$ was obtained since no $CH_4$ peak was observed above 670 K.

As was mentioned earlier, dual temperature experiments can also be carried out after chemisorption of $CH_4$ at moderate temperatures. The temperature gap is however necessarily narrower in this case than in the one examined by Koerts et al.[9], in which it was usually greater than 350 K. Significantly enough, the resulting total production of the $C_{2+}$ alkanes does not always increase when $T_2$ decreases, since the reverse is observed on Pt. What is most sensitive to the lowering of the hydrogenation temperature is the distribution of the products, the higher alkanes being favored at low hydrogenation temperatures. A tentative interpretation of this behavior consists in assuming that, at each temperature and at a given

coverage, different species exist *at (or near) equilibrium*. The cooling of the sample should thus result in a state of higher aggregation of the adspecies.

Another striking difference between both set of results lies in the fact that *many more alkane species* are produced *after adsorption at a moderate temperature* (more than 30 different alkanes can be identified) than after decomposition to carbon at a much higher temperature. Moreover, in general the *Anderson–Schulz–Flory distribution is largely disobeyed*. As is well known the ASF distribution is the result of a kinetic mechanism in which every precursor on the surface can either desorb or continue its growth according to probabilities that do not depend upon the length of the growing chain. The hydrogenation involving the C deposits formed at a high temperature may be assumed to take place in approximately such a situation since C–C bonds must be formed in parallel with removal of hydrocarbons. However C–C bonding occurs in quite a different way following methane adsorption at a moderate temperature, since the $C_{2+}$ precursors are the final products of this first step. As such, they are subjected (among other factors) to the requirements of the surface geometry which can favor a particular clustering of $C_1$ units (as $C_5$, for example) as well as certain shapes of clustering (cyclo-$C_5$ instead of n-$C_5$).

Another consequence of exposing the metal to $CH_4$ at a moderate temperature is that *more reactive carbon is expected to be formed and repetition of uninterrupted cycles can be carried out with sustained activity* as already reported [6].

In summary, despite certain similarities, both procedures differ fundamentally in their underlying chemistry because exposure of the metal to $CH_4$ at $T \geq 723$ K mainly results in elemental C deposition or carbide formation whereas dehydrogenating chemisorption occurs at moderate temperatures (373–573 K) with a build-up of $C_xH_y$ surface species. However the analysis of the latter procedure has to be placed on a more quantitative thermodynamic basis in order to understand why $C_{2+}$ alkanes (whose formation from $CH_4$ implies a loss of $H_2$) can be obtained in the second stage (therefore in large excess of $H_2$) at pressures which are higher by several orders of magnitude than what would at first sight be expected at equilibrium under such conditions.

## 5. Thermodynamic analysis of isothermal cycles

The first step of $CH_4$ chemisorption can be represented by:

$$CH_4 + 2^* \leftrightarrows CH_{3\,ads} + H_{ads}$$

As $H_2$ is evolved during the exposure to $CH_4$, formation of $CH_x$ species with $x$ possibly lower than 3 can be assumed. On the basis of the amount of $H_2$ evolved and on that of $CH_4$ chemisorbed [inferred from temperature-programmed desorption (TPD) and TPSR experiments as above-mentioned], $x$ values ranging from 3 to 0 could be determined and therefore gave support to the occurrence of the following processes:

$$CH_{3\,ads} + ^* \leftrightarrows CH_{2\,ads} + H_{ads}$$

and so on, as well as:

$$H_{ads} + H_{ads} \leftrightarrows H_2 + 2^*$$

C–C bond formation is expected to occur between neighboring $CH_x$ groups. No hydrocarbon leaves the surface during exposure to $CH_4$ (except for ethane, in the case of Pt), most probably because, in the absence of $H_2$, their precursors would have to be removed as olefins or alkynes and are thus too strongly bound to the surface. Fresh $H_2$ is therefore required to remove them. However, more dehydrogenation than stoichiometrically required by the homologation occurs during the exposure to $CH_4$ as can be seen from the low values of $x$. A smaller quantity of hydrogen than that removed in the first step is therefore absorbed by the adspecies in the second step but it must be supplied at a much higher pressure.

Focusing our attention on the example of ethane which has to be formed through association of two adspecies, the first step can be summarized as:

$$2CH_4 + 2^* \rightarrow C_2H_{n\ ads} + \left(4 - \frac{n}{2}\right)H_2 \quad (low\ pressure) \qquad (1)$$

whereas the second one can be represented by:

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

so that the overall process is:

$$2CH_4 + \left(4 - \frac{n}{2}\right)H_2\ (1\ bar) + 2^* \rightarrow C_2H_6 + 2H_{ads} + \left(4 - \frac{n}{2}\right)H_2\ (low\ pressure) \qquad (\mathbf{A})$$

The latter equation expresses the material balance in the case of an initially clean surface exposed in turn to $CH_4$ and $H_2$. However in a series of uninterrupted cycles, $CH_4$ does not contact empty sites but hydrogen-covered sites instead, liberating some of this hydrogen. Therefore more hydrogen than in the empty-site case will be removed from the surface and will be carried away by the flow of $CH_4$. In such conditions the balance of the first step becomes:

$$2CH_4 + 2H_{ads} \rightarrow C_2H_{n\ ads} + \left(5 - \frac{n}{2}\right)H_2 \quad (low\ pressure) \qquad (1')$$

and the global balance becomes:

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

In the foregoing 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 considered as equivalent to the sum of the following three processes:

$$2CH_4\ (1\ bar) \rightarrow C_2H_6\ (1\ bar) + H_2\ (1\ bar) \quad \Delta G_3^0 > 0 \qquad (3)$$

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

$$H_2\ (1\ bar) + 2^* \rightarrow 2H_{ads} \neq \Delta G_5^0 > 0 \qquad (5)$$

and case **B** to the sum of the following two:

$$2CH_4\ (1\ bar) \rightarrow C_2H_6\ (1\ bar) + H_2\ (1\ bar) \quad \Delta G_3^0 > 0$$

$$\left(5 - \frac{n}{2}\right)H_2\ (1\ bar) \rightarrow \left(5 - \frac{n}{2}\right)H_2\ (low\ pressure) \quad \Delta G_6 < 0 \qquad (6)$$

Only in case **A** could the $H_2$ evolved from the surface be monitored unambiguously because in case **B** it was impossible to discriminate clearly between the $H_2$ simply removed from the empty space of the reactor and that actually removed from the surface. Let us consider therefore case **A**, which does not modify the meaning of the present approach. Common average values of the $H_2$ pressure during the first step taking place on an initially clean surface were lower than $5 \times 10^{-4}$ bar. At a typical temperature of 500 K this causes a value of $\Delta G_4$ (or $\Delta G_6$) of $-31.5$ kJ/mol at a conservative estimate. If we now make the reasonable assumption that the $C_2$ precursor is formed by the binding of two $CH_x$ units and as $x$ commonly equals 2 for very short exposures and 1 for longer ones, we can take 4 as the maximum reasonable value of $n$ (in $C_2H_n$). This results in $\Delta G_4 = -63$ or $-94.5$ kJ, compared with $+70.5$ kJ for $\Delta G_3^0$ (free enthalpy of homologation). Moreover, in case **A**, the energy of adsorption is added to the expansion energy. We can therefore conclude that the free energy supplied by the expansion process of $H_2$ can, completely or for the most part, explain the formation of ethane at

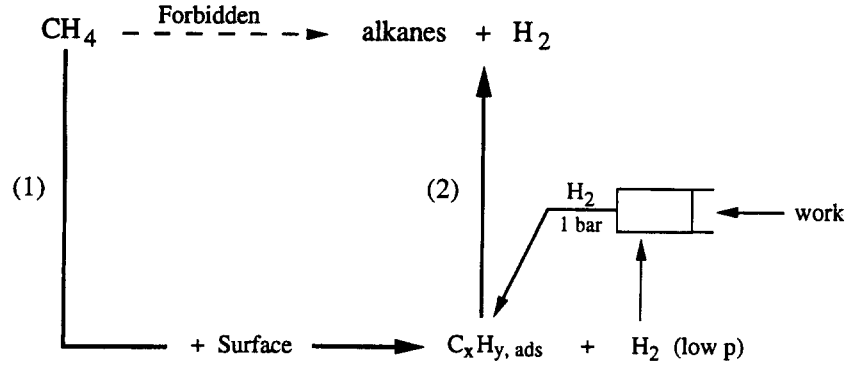


Fig. 8. Schematic representation of how the thermodynamic barrier is overcome in the isothermal two-step homologation of methane.

1 bar. In case **B**, the energy of adsorption does not appear explicitly but the amount of $H_2$ expanded is higher by one mole. This stems from the fact that in the first step all the $H_2$ (including that simply adsorbed during the second step of the preceding cycle) is removed at low pressure, whereas the coverage of the surface during each hydrogenation step is effected at 1 bar. We can therefore conclude that $C_2H_6$ can be removed even at 1 bar (and even at a higher pressure).

That the whole process becomes possible clearly results from the fact that the $H_2$ produced by the homologation is freed at low pressure instead of being obtained at 1 bar as is implied by writing:

$$2CH_4 \rightarrow C_2H_6 + H_2$$

$$\Delta G^\circ = +70.5 \text{ kJ mol}^{-1}$$

This *separate* removal of $H_2$ at low pressure and the consequent production of ethane at possibly ordinary pressure is in fact what the forced feed cycling of the catalyst enables us to do. We can rephrase this conclusion in an equivalent way by noticing that the whole process would require no supply of fresh hydrogen at 1 bar if the $H_2$ which is freed during the first step was recovered and compressed to 1 bar before being re-introduced into the reactor. This is represented in Fig. 8. The necessary expenditure of mechanical work represents the amount of energy required to overcome the thermodynamic barrier.

This analysis can easily be extended to the formation of other higher alkanes. Increasing molar energy barriers have to be overcome with the increasing range of every concerned alkane but this is balanced by the higher quantities of hydrogen involved and the corresponding higher mechanical energy which has to be supplied.

## 6. Concluding remarks

Three final remarks need to be made.

### *6.1. Has the word 'catalyst' been used in its strict sense?*

Obviously the whole process is not catalytic in nature since it consists of two successive *stoichiometric* reactions: first, adsorption and C–C bond formation and second, hydrogenation. One important feature of true catalysis remains however since the metal surface is restored at the end of each cycle. Furthermore it can of course be added that the various elementary processes of which the overall transformation is composed could not proceed on surfaces which would differ from those of the transitions metals commonly used as catalysts of reactions involving hydrocarbons and hydrogen. We therefore conclude that the word 'catalyst' is not really misused even though the term 'catalysis' might best be avoided.

### *6.2. Comparison of the present forced feed cycling with that usually referred to in other cases*

Forced feed cycling is commonly carried out for bimolecular reactions by alternately cycling

the feeds of each reactant to the catalyst. In the present case, the situation is quite different since the catalyst is periodically fed by $CH_4$ which is the only reactant or with fresh $H_2$ which can be considered as one of the products after adequate compression. Puzzling as it may appear at first sight, this procedure has been shown to overcome the thermodynamic barrier.

### *6.3. Possible contribution of the mechanistic analysis of the present system to the understanding of related continuous or forced cyclic reactions with no thermodynamic constraint*

The mechanistic analysis presented above, even if not developed in detail, stresses the fact that if one of the reactants is a sufficiently complicated molecule (especially an hydrocarbon) the fate of this molecule on the surface can be fundamentally different depending on whether the second reactant is simultaneously present or not. Clearly the presence of this other reactant is expected to hinder numerous processes into which the molecule considered and its derived species could be involved. Very different selectivities can therefore result between the steady co-feeding and the forced cycling of the catalyst.

This remark applies to systems that are related to the present study even if they are not thermodynamically constrained. Let us consider for instance a mixture $C_2H_4/H_2$ which, on all metals used as hydrogenation catalysts, leads essentially and often exclusively to $C_2H_6$. On Ru, reaction to $C_{3+}$ products was reported by Jordan and Bell [21] but at a low conversion since less than 4% of the reacted $C_2H_4$ was homologated to $C_{3+}$ hydrocarbons at 493 K, $H_2/C_2H_4$ ratios ranging from 1/8 to 1/1 at a $C_2H_4$ pressure of 0.40 bar. When $^{13}CO$ was added so that the resulting mixture of $C_2H_4$, $H_2$ and $^{13}CO$ was 2:2:1, hydrogenation of $C_2H_4$ to $C_2H_6$ was suppressed but conversion to homologated products increased significantly. Most remarkably only $C_2H_4$ contributed to the formation of $C_{3+}$ alkenes and alkanes for the preceding mixture composition while the reacted CO led to propanal and some 1-propanol.

Formation of higher alkenes and alkanes from ethylene is a thermodynamically favored process. From the considerations developed in the present article concerning the possibility of C–C bonding between neighbor H-deficient $CH_x$ units, association of $C_2$ units and homologation should be expected. No hydrogen is required by homologation to higher alkenes but homologation was not observed by Jordan and Bell in the absence of $H_2$ most probably because the alkenes are too strongly adsorbed. Introducing $H_2$ into pure $C_2H_4$ allowed them to observe the formation of a small amount of homologated species but also showed the difficulty inherent in hydrogenating to ethane at a much higher conversion than homologation. A reasonable interpretation of the role of CO is that it efficiently hinders the chemisorption of $H_2$ (as is well known in Fischer–Tropsch synthesis) and accordingly favors binding between $C_2$ units. CO can therefore be viewed as allowing the $C_2H_4$ molecules to arrange themselves into a surface configuration resembling what would be found in the absence of $H_2$.

The absence of $H_2$ and the exposure of the metal catalyst to pure $C_2H_4$ would be expected to maximize homologation even if the homologated species remain in the adsorbed state. For such a case, self-hydrogenation of part of the adsorbed $C_2H_4$ leading to desorbed $C_2H_6$ and to an equal amount of adsorbed $C_2H_2$ was already reported to occur on Ni at room temperature by Jenkins and Rideal [22]. Such a process, impossible in the presence of $H_2$, may be expected to make homologation even easier. Substantial homologation of $C_2H_2$ in $C_2H_2/H_2$ mixture was indeed already observed by Sheridan over Ni [23]. Spectroscopic evidence of the existence of oligomers on the surface of Ni after adsorption of $C_2H_4$ at room temperature was first reported by Eischens and Pliskin [24]. This conclusion was then extended to Pt [25]. However removal of these species requires a supply of $H_2$ to make them desorb as alkanes. This formation of higher alkanes by successive exposures of metal films to $C_2H_4$ and $H_2$ was first published by Beeck [26] who reported obtaining 90% of $C_4$–

$C_8$ alkanes and 10% only of $C_2H_6$ on Ni at room temperature. Mainly n-butane was obtained later in a similar experiment conducted on Pt at room temperature. We have just reported [19] the results of similar experiments carried out on EUROPT-1 with $C_2H_4$ and $H_2$ under various conditions which showed that more than 50% of the adsorbed $C_2H_4$ can be converted to alkanes ranging from $C_3$ to $C_8$ (most of them with an even number of C atoms). This is clear confirmation that, in the surface chemistry of catalysts, forced feed cycling can open up novel synthesis routes different from those permissible under steady co-feed conditions. Forced feed cycling thus deserves more study than has so far been granted to it.

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