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RESEARCH NOTE

Formation of Higher Hydrocarbons by Hydrogenation of the Adspecies Preliminary Formed on EUROPT-1 upon Exposure to a CH_4 Dose

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It is now well known that higher hydrocarbons can be formed by feeding certain supported (or bulk) metal catalysts with CH_4 and H_2 successively (1–15). In our own contributions to this subject we have insisted that more hydrogen was released during the first step than that stoichiometrically corresponding to the hydrocarbons formed during the further hydrogenation step. However, we have also shown that, in our *isothermal* procedure, it is a thermodynamic requirement that H_2 be used in the second step at a pressure higher than that at which it is released in the first step (13). We have also shown that the amount of higher hydrocarbons obtained is strongly dependent upon the flow rate of CH_4 during the first step and we have explained that the reason of this dependency is that the flow of CH_4 acts as a dehydrogenating agent by conveying the desorbed H_2 out of the reactor. Exposure to *static* CH_4 does not allow efficient removal of H_2 and only results in vanishing amounts of higher hydrocarbons in the further hydrogenation. Accordingly, due to the large quantity of methane flushed through the catalyst during the first step, the yield of the overall conversion, expressed on the basis of the incoming methane, has always been very low in our attempts as in those having used the same mode of exposure to CH_4.

Contrasting with this situation, Koerts *et al.* reported a yield of 13% obtained on 300 mg of a 5 wt% silica-supported Ru catalyst by feeding it with a mixture of He and 0.28% CH_4 at 450°C for 3 min (corresponding to 4.57 μmol of CH_4 given to the catalyst) and hydrogenating the resulting adspecies at 95°C (4). The corresponding amount of surface carbon was estimated to 2.66 μmol with a fraction of 21% (0.56 μmol) being converted to C_{2+} species. This sizable yield may be ascribed to what was considered as a thermodynamic requirement by the authors, namely the large difference between the temperatures of the two reaction steps.

The purpose of the present paper is to report a sizable yield of methane conversion obtained by submitting the catalyst to an *isothermal* sequence at a *moderate* temperature and by using a small dose of CH_4 at ordinary pressure. It is also to identify the conditions required for substantially increasing the yield of this reaction sequence.

Our catalyst sample consists of 100 mg of EUROPT-1, which is a 6.3 wt% Pt supported on silica (16). The main features of the apparatus and the preliminary treatments of the catalyst have already been described (13–15). Doses of CH_4 are sent to the catalyst by using a set of three valves represented in Fig. 1 and possibly fed with purified gases (CH_4, He, and H_2 from two different lines, H_2 (1) and H_2 (2)). Valve 2 is equipped with one of four loops of known capacities (0.45, 0.60, 4.6, or 8.8 cm^3). Handling the valves as indicated in Fig. 1 allows us to submit the catalyst to the sequence He, CH_4, and H_2 by successively feeding the reactor with:

(i) a flow of H_2 (H_2 (1)) to reduce the catalyst or to clean its surface while feeding the loop with CH_4,

(ii) a flow of He to desorb and remove H_2,

(iii) the dose of CH_4, pushed by H_2 (H_2 (2)) which reacts the adspecies off the surface. H_2 (2) flow and what remains of the CH_4 dose are then directed towards a trap (liquid air temperature) condensing the C_{2+} products and some CH_4. H_2 (2) flow is maintained for 10 min in order to evaporate most of the methane and so to make the further analysis of the ethane easier.

The total content of the trap is then evaporated and chromatographically analyzed as a whole.

As reported previously (13), a constant C_{2+} production was obtained when this catalyst was submitted to as much as 30 repeated CH_4/H_2 sequences involving exposures to CH_4 even longer than most of those carried out in the present work. Despite this evidence of no visible carbon contamination undergone by the Pt under more severe conditions, in the present study the catalyst has been restored to the same initial clean state, before each new exposure to CH_4, by heating it up to 400°C in a flow of H_2, substituting He for

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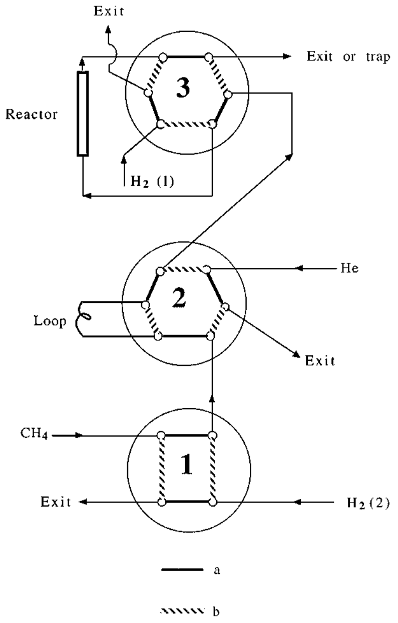

FIG. 1. Set of valves allowing the catalyst to receive a flow of He, followed by a dose of CH_4, then a flow of H_2: (i) 1 (a)/2 (a)/3 (b): reduction of the catalyst by H_2 (1) and filling of the loop with CH_4. (ii) 1 (a)/2 (b)/3 (b): closure of the CH_4 loop and arrival of He up to valve 3, followed by: 1 (b)/2 (b)/3 (a): purge of the reactor by He and arrival of H_2 (2) up to valve 2 (CH_4 loop still closed). (iii) 1 (b)/2 (a)/3 (a): pushing of the CH_4 dose to the reactor by H_2 (2) whose flow is maintained for 10 min.

H_2 to remove adsorbed hydrogen and, finally, cooling it to the desired temperature. Only negligible quantities of CH_4 are removed during the heating in H_2. All the results given hereafter are obtained with a good reproducibility (±5%).

In the present mode of exposure of the catalyst to CH_4, the residence time of the dose, which is also the duration of exposure to CH_4 (defined as the quotient of the dose capacity by the flow rate of the pushing H_2) can be varied by choosing either the size of the dose of CH_4 pushed by a given flow rate of H_2 or the flow rate of H_2 pushing a given dose of CH_4 to the catalyst sample.

Our first set of results (see Fig. 2) shows what happens, at 260°C, when the dose of CH_4 is kept constant while its residence time is varied due to the adequate choice of the H_2 flow rate. A second set (Fig. 3) is related to the other way of fixing the residence time.

In Fig. 2 the results are represented in four couples of plots, each of them being related to a fixed dose of CH_4. The variations as well of the total amount of homologated CH_4 as of the quantity of each higher hydrocarbon versus the duration of the exposure to CH_4 are given. Mainly C_2–C_4 alkanes are produced and ethane is by far the major product. There are also small amounts of pentanes and traces of hexanes (2,3-dimethylbutane and 3-methylpentane). A first remarkable observation is that the ethane production, and consequently the total C_{2+} production, is maximized at very short contact times. A second observation is that, surprisingly, the amount of homologated CH_4 is not significantly lower than those obtained during hydrogenations following much longer exposures as those previously reported (1, 13, 14). However, two major differences with respect to these previous results must be underlined. The ethane, possibly formed *during* the exposure to CH_4 and carried away with what remains of the dose, is here trapped with the products of the second step and is therefore included in the total C_{2+} production. Moreover, the product distribution is strongly shifted to the lighter alkanes (mainly ethane).

Due to the much lower quantity of CH_4 sent to the catalyst, its conversion to higher alkanes can reach much higher values than those previously obtained on the same catalyst

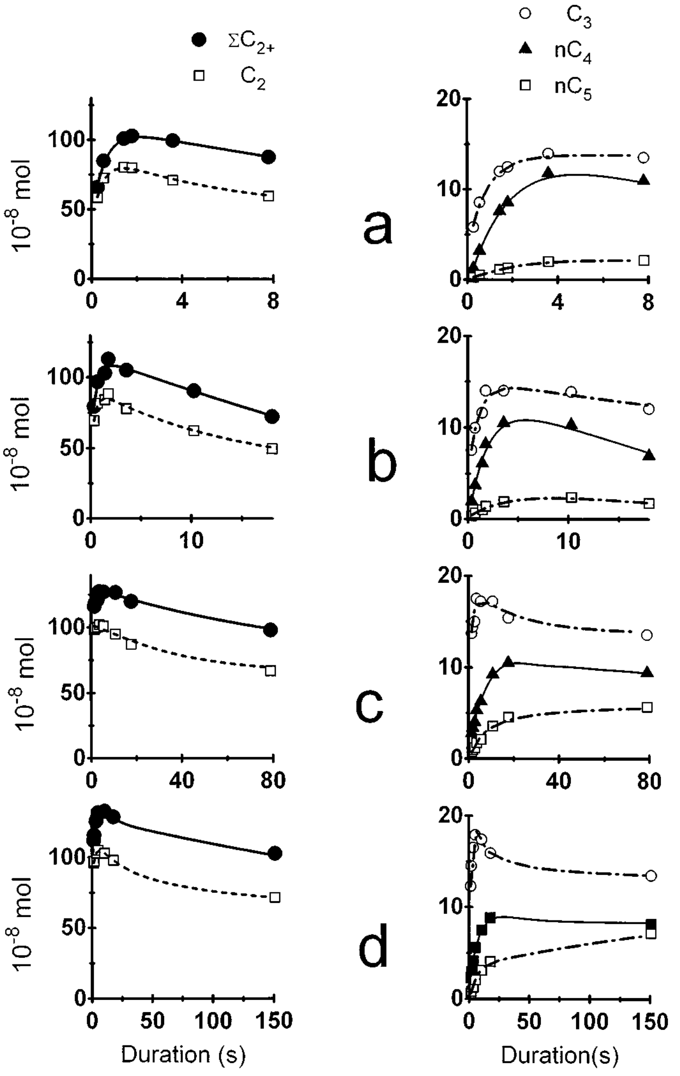

FIG. 2. Variation of the quantities of higher hydrocarbons resulting from the exposure of the catalyst to a fixed dose of CH_4 and further hydrogenation of adspecies, versus the duration of exposure controlled by the flow rate: The quantities refer to the carbon content of each product; Temperature: 260°C; CH_4 dose: 0.45 cm^3 (a); 0.60 cm^3 (b); 4.6 cm^3 (c); or 8.8 cm^3 (d).

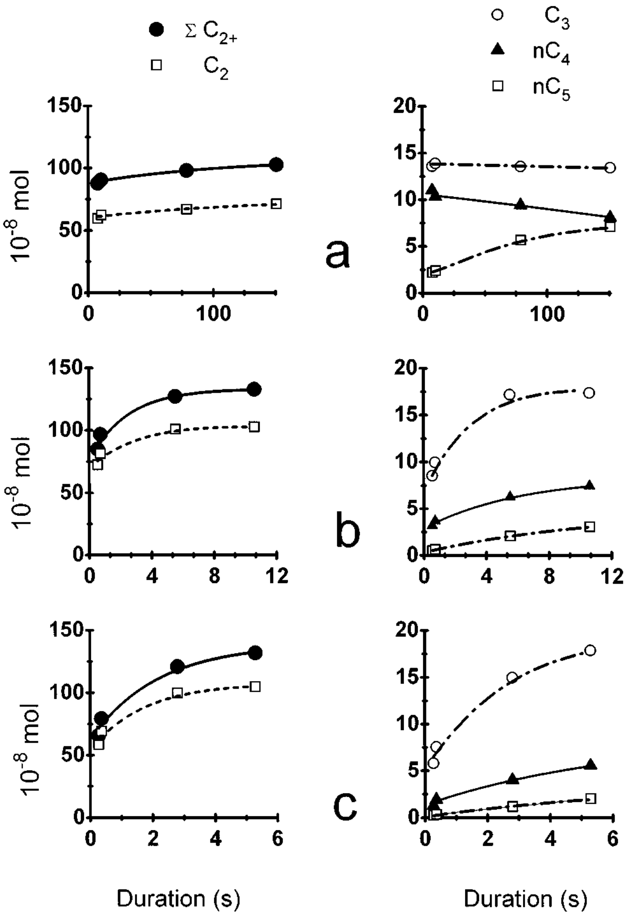

FIG. 3. Variation of the quantities of higher hydrocarbons resulting from the exposure of the catalyst to a dose of CH_4 and further hydrogenation of adspecies versus the duration of exposure controlled by the size of the dose at a fixed flow rate: The quantities refer to the carbon content of each product; Temperature: 260°C; H_2 flow rate: 3.5 cm^3/min (a); 50 cm^3/min (b); or 100 cm^3/min (c).

(13). The best yield is thus equal to 5.8% with the 0.45 cm^3 dose, which is all the more noticeable that no more than half of the methane dose could have been chemisorbed, due to the limited monolayer capacity of the catalyst sample. Improved yield could have been obtained by using more catalyst. In addition, some H_2 can have diffused into the small CH_4 dose, which can but hinder the C–C bonding processes. Let us recall that the thermodynamically permissible yield of the CH_4 conversion into ethane and hydrogen is 0.033% at 260°C. We have already explained why higher yields can be reached, due to the two-step procedure (13).

In Fig. 3 the results are represented in three couples of plots, each of them being related to a fixed H_2 flow rate which was successively set to 3.5, 50, and 100 cm^3/min. On each couple of plots, each point corresponds to one of the four possible sizes of the CH_4 dose. At a fixed H_2 flow rate, only increasing productions are obtained as a function of the residence time of the dose, except for the formation of butanes which, at the smallest flow rate, decreases with the duration of exposure at the profit of the C_5's. The total C_{2+} production quickly levels up versus the exposure duration, the longest period of increase being displayed by the pentanes.

In order to know the nature and the quantity of the hydrocarbons possibly released into the CH_4 dose itself, during the residence of the latter in the catalyst bed, we have pushed the methane dose with He, instead of H_2, in experiments otherwise unchanged with respect to the preceding ones. These attempts were carried out only with the 8.8-cm^3 dose, pushed by He flowing at 50 cm^3/min for 20 s. The residence time of CH_4 was fixed at $\approx$10 s. Only formation of a small amount of ethane ($\approx 8 \times 10^{-8}$ mol) and of traces of propane took place in the absence of H_2, which is clear evidence that there is little contribution ($\leq$10%) of the products formed during the exposure to CH_4 in the preceding experiments.

The maxima displayed by most of the curves represented in Fig. 2 at short, or very short, residence times of the CH_4 dose are surprising because the surface coverage can but increase upon prolongation of the exposure of the metal surface to the methane. However, it must be kept in mind that, in the experiments corresponding to this figure, the residence time of CH_4 has been fixed by adjusting the flow rate of the pushing H_2 to the desired value. Longer residence times, resulting in rising coverages, require lower H_2 flow rates and thus also result in longer residence times of the heavier hydrocarbons released in the further hydrogenation. Therefore, these products are increasingly submitted to hydrogenolysis upon enlargement of the residence time, whence the observed maxima. In support to this interpretation, we can remark that no maxima are displayed by the curves of Fig. 3 because, in the corresponding experiments, the increases of the residence time result from those of the CH_4 dose at a *constant H_2 flow rate.*

Obtaining of C_{2+} productions close to those previously reported (1, 13, 14) despite the strong shortening of the exposures to CH_4 constitutes a meaningful feature of the system under study since it clearly shows that as much methane can be converted as previously but in much less time. However, what must also be noticed is that the difference lies mainly in the product distribution which is, here, strongly shifted towards the lighter products, mainly ethane. From Fig. 2c or Fig. 3a we can see that the pentanes represent ca 5% of the C_{2+} production corresponding to a 1-min exposure, whereas in our preceding report concerning the same catalyst (13) the C_5 to C_8 hydrocarbons amounted to about 25% for an exposure of the same length and at the same temperature. That is clear indication that, even if the slow step of the reaction of CH_4 with the Pt surface is the CH_4 chemisorption, this step is not the only time-consuming step. Fast equilibrium between H_2 desorbed during exposure to CH_4 and the hydrocarbonaceous adspecies does not prevent the corresponding H_2 pressure from being low and the more so as the H-deficiency of the adspecies increases, whence the necessary lengthening of the exposure to CH_4 if products of higher weight than ethane are desired. This requirement constitutes a *key factor* of the system and necessarily results in negligible conversion of the incoming methane if a flow of the latter is used to remove the desorbed H_2 from the reactor as done in our preceding attempts. In the present study, all the H_2 removed is necessarily contained in the volume of the CH_4 dose (0.45 to 8.8 cm^3). The amount of CH_4 used is almost negligible, as compared to that involved previously (1-min exposure at a flow rate of 400 cm^3/min), which prevents the adspecies from losing as much hydrogen as they would have if this hydrogen had been diluted in a larger volume. The present conditions therefore result in the formation of less H-deficient adspecies and, accordingly, to lighter products. Consequently, *our means of increasing the overall yield also shifts the distribution towards the lighter products*.

We can reasonably deduce that some *optimum H-deficiency* has to be ascribed to the adspecies in order to get a substantial proportion of products heavier than C_2H_6. If too high temperatures must be avoided for not favoring the formation of bad carbon, the adequate H_2 removal needs a sufficiently prolonged exposure to CH_4 with continuous H_2 withdrawal. The additional target of improving the yield compels us to find another means of removing H_2 than merely conveying it out of the reactor by the flow of CH_4. Exposure of the catalyst to *static* CH_4 with simultaneous *in situ* removal of the desorbed H_2 should be envisioned. Use of a membrane, as recently proposed by Garnier *et al.* (17), might be an appropriate way of solving the problem.

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