# Carbon monoxide induced desorption of alkanes and alkenes up to $C_8$ after chemisorption of methane on platinum

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$CH_4$ homologation can proceed under reductive conditions by successive exposures of various supported metals to $CH_4$ and $H_2$. When a $Pt/SiO_2$ catalyst is submitted to a CO dose after an exposure to $CH_4$ at a moderate temperature, several hydrocarbons are released with a large proportion of olefins. It may therefore be concluded that C–C bonding processes take place during the mere exposure of platinum to $CH_4$ at moderate temperatures.

**Keywords:** methane; chemisorption; methane chemisorption; methane oligomerization; precursors of higher hydrocarbons; hydrocarbonaceous adspecies

## 1. Introduction

We have recently reported that homologation of methane can be obtained via an isothermal two-step procedure consisting of successive exposures of transition metal catalysts to flowing $CH_4$ and $H_2$ at temperatures depending upon the metal and ranging typically from 100 to 300°C [1–3]. We have interpreted these observations by the formation of $CH_x$ species upon $CH_4$ chemisorption whereas the parallel release of $H_2$ results into H-deficiency of these species and into their correlative ability to give rise to C–C bonding processes. Alkanes are subsequently removed by further subjecting to $H_2$ of the so formed surface $C_{2+}$ precursors.

In line with these views we have found it reasonable to search for a possible insertion of CO into the adspecies and for the possible subsequent release of oxygenates by $H_2$. Here, we report that such an insertion of CO does not appear possible since no oxygenates are obtained neither in the $CH_4/CO$ nor in the $CH_4/CO/H_2$ sequence. However, desorption of numerous alkanes and alkenes is unexpectedly induced by CO.

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## 2. Experimental

### 2.1. CATALYST

Our catalyst sample consists of 100 mg of EUROPT-1 [4] (6.3 wt% Pt dispersed on Aerosil), placed in a continuous flow fixed bed reactor made of a U-shaped quartz tube (4 mm i.d.). Pt is initially reduced in flowing $H_2$ (50 $cm^3/min$) during a slow ramp of temperature (1 K/min) up to 400°C at which temperature it is maintained in the $H_2$ flow for 1 h. In order to remove hydrogen, it is then fed with a flow of He (50 $cm^3/min$) for 30 min and is finally cooled in the flow of He at the desired temperature of experiment.

Between two experiments the catalyst is first submitted to a flow of $H_2$ (50 $cm^3/min$) for 1 h at 400°C in order to remove any carbonaceous residue and then to a flow of He as in the initial treatment.

### 2.2. APPARATUS AND PROCEDURE

The apparatus, already described [2], essentially allows us to feed the catalyst with pure $H_2$, He, CO or $CH_4$ and to analyze the products of $CH_4/H_2$, $CH_4$/He or $CH_4$/CO sequences.

$CH_4$ (N45 Air Liquide) contains no detectable amount of any other hydrocarbon ($<0.1$ ppm). It is purified from $O_2$ traces through an oxytrap and from water traces through molecular sieve. $H_2$ and He are purified from $O_2$ and any condensable impurity, whereas CO (N45 Air Liquide) is used as received.

After exposure to methane, the catalyst is submitted to a flow of $H_2$ or He or receives a dose of CO followed by a flow of He or $H_2$, which results in the removal of various amounts of different hydrocarbons. Prior to its sending to the catalyst, the CO dose is contained in the loop of a six-port sampling valve from which it is pushed forward by the appropriate gas at the end of the exposure to $CH_4$. All the products leaving the reactor are condensed in a trap filled with glass beads and cooled in liquid air. Among all the products, only methane is not completely condensed and its evaporation is continued on purpose by flushing the trap with helium. Thus, the content of the trap is enough depleted in $CH_4$, which improves the chromatographic analysis of the $C_2$'s. The trap is then heated to ca. 300°C and all the products are introduced into one of two possible chromatographic columns, A or B. Column A (graphitized black; i.d.: 2.1 mm; $l$: 2 m) is best suitable for the separation of the alkanes and column B (chromosorb impregnated with 23% SP1700; i.d.: 2.1 mm; $l$: 5 m) for the separation of the alkenes. Column A is initially maintained at 50°C for 5 min and then regularly heated to 220°C within 6 min. Column B is initially maintained at 50°C for 2 min and then heated to 110°C within 2 min. Discrimination between the alkanes and the alkenes produced in the $CH_4$/CO sequence requires repetition of each experiment and analysis of its corresponding products through either column A or column B. The effluent of column A or B is directed to a third column, C (molecular sieve, r.t.), devoted to the trapping of the $C_2$'s. After elution and trapping of the $C_2$'s, column C is by-passed until the analysis of the highest products is completed. Thereafter column C is switched on and heated at 175°C in order to carry out the analysis of the $C_2$'s.

## 3. Results

As already reported and as exemplified in table 1 (a) alkanes are the only products of the $CH_4/H_2$ sequences. No appreciable formation of alkanes higher than $C_6$ result from exposures to $CH_4$ during 30 s at either 250 or 300°C.

As will be reported elsewhere, desorption of $CH_4$ occurs when $CH_4$ is switched to He. There is no spontaneous desorption of any higher hydrocarbon. Even if the duration of the He feed is short (1 s or so), which can be done by placing a dose of He between $CH_4$ and $H_2$, the quantity of the desorbed $CH_4$ cannot be negligible and must cause some dissociation of part of the $C_{2+}$ precursors since significantly lower amounts of $C_{2+}$ alkanes are released upon the subsequent hydrogenation.

Carrying out the ternary sequence $CH_4/CO/H_2$ at 250°C with a 1.4 $cm^3$ dose of CO at 1 bar after a 30 s exposure to $CH_4$ (flowrate 110 $cm^3/min$) produces a total amount of the $C_{2+}$ hydrocarbons equivalent to only 0.81 μmol of $CH_4$ instead of 1.07 μmol for the corresponding $CH_4/H_2$ sequence. Such a decrease of the total production is not so surprising because the sending of a CO dose to the catalyst also implies suppressing $CH_4$ for a while before feeding with $H_2$, just as in the case of a short volume of the He placed between the flows of $CH_4$ and $H_2$. What is more unexpected is the extra-formation of olefins as well as that of hydrocarbons possibly higher than those formed in the absence of CO, which is in fact the consequence of contacting the metal with a dose of CO after preliminary chemisorption of $CH_4$ (table 1 (b)). Acetylene, propadiene and butadienes are absent. Alkynes and poly-olefins are accordingly supposed to be absent from the higher hydrocarbons released by CO. No oxygenates can be evidenced either. Fig. 1 clearly shows that, compared to the corresponding alkenes, the alkanes released in a dose of CO at 250°C are more and more favored as their molecular weight increases. At 300°C, sending a CO dose unfavors the $C_2$–$C_4$ hydrocarbons but favors the highest ones and the olefins especially. For example, the selectivities to the $C_6$- and $C_8$-alkenes equal 8.14 and 29.5% respectively and there are nearly no $C_5$–$C_8$ alkanes.

Dilution of CO with He does not change the nature of the products but causes a decrease of the quantity of each of them, as can be seen in table 1 (c), which clearly shows that desorption in CO is much more efficient than the mere spontaneous desorption taking place in He. When hydrogenation is performed after the sending of the dilute (1/1) (He, CO) dose, the total amount of the $C_{2+}$ hydrocarbons is found to be the same as in the case of undilute CO. The influence of the partial pressure of CO is well displayed in table 2. A double dose of CO displays but a little sup-

Table 1
Nature and quantities[a] of the $C_{2+}$ hydrocarbons formed upon hydrogenation or short exposures to CO after preliminary chemisorption of methane[b]

| | $C_2$ | | $C_3$ | | $C_4$ | | $C_5$ | | A | $C_6$ | | B | $C_8$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | sat. | = | sat. | = | sat. | = | sat. | = | | sat. | = | | = | |
| *250°C* | | | | | | | | | | | | | | |
| $CH_4/H_2$ (a) | 65.3 | – | 23.6 | – | 9.70 | – | 7.20 | – | – | 1.60 | – | – | – | 107 |
| $CH_4/CO$ (b) | 33.2 | 7.22 | 4.71 | 3.66 | 1.56 | 2.78 | 0.24 | 1.74 | 0.15 | – | 1.13 | – | 1.38 | 57.8 |
| $CH_4/(CO,He)$ (c) | 30.1 | 4.43 | 5.37 | 3.01 | 1.80 | 2.54 | 0.40 | 1.70 | 0.10 | – | 1.10 | – | 1.40 | 51.9 |
| *300°C* | | | | | | | | | | | | | | |
| $CH_4/H_2$ (a) | 71.3 | – | 20.9 | – | 15.5 | – | 23.7 | – | – | 2.70 | – | – | – | 134 |
| $CH_4/CO$ (b) | 15.6 | 2.65 | 2.02 | 0.79 | 0.84 | 0.62 | 3.85 | 6.17 | 0.23 | – | 4.34 | 0.51 | 15.7 | 53.3 |

[a] The quantities are expressed in $10^{-8}$ mol of the equivalent amounts of $CH_4$; sat.: saturated; =: alkene(s); $C_4$ sat.: $i$-$C_4$ + $n$-$C_4$; $C_4$=: 1-butene + $i$-butene + 2-butene (cis + trans); $C_5$ sat.: $i$-$C_5$ + $n$-$C_5$ + cyclo$C_5$; $C_5$=: 1-pentene + 2-pentene (cis) + 2-methyl-2-butene + cyclopentene; A: unresolved mixture of 2,2-dimethylbutane + 2-methyl-1-butene + 2-pentene (trans); $C_6$ sat.: $n$-$C_6$ + two unidentified branched hexanes; $C_6$=: unidentified hexene + 1-methyl-cyclopentene; B: unidentified $C_7$ or $C_8$; $C_8$=: unidentified octene.

[b] (a) Exposure to $CH_4$ (110 $cm^3$/min) at 250 or 300°C for 30 s followed by 15 min hydrogenation in a flow of 50 $cm^3$ $H_2$/min. (b) The same exposure to $CH_4$ is followed by a dose of 1.4 $cm^3$ (ambient pressure) of CO. (c) The same experiment as (b) except for the CO dose: 1.4 $cm^3$ of (He, CO) (1/1).

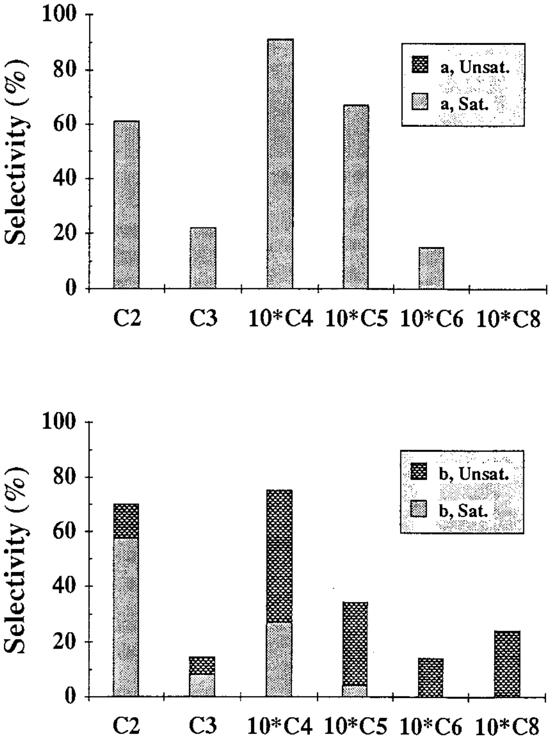

Fig. 1. Distribution of the $C_{2+}$ hydrocarbons produced in the sequences (a) and (b) (250°C) of table 1.

Table 2
Major products desorbed at 250°C in a dose of CO after exposure to $CH_4$

| Product | Quantity[a] of product obtained by sending a dose of (He, $x$% CO) | | | |
|---|---|---|---|---|
| | $x = 10$ | $x = 25$ | $x = 50$ | $x = 100$ |
| ethane | 18.1 (96.28) | 26.1 (61.70) | 30.1 (58.0) | 33.2 (57.4) |
| ethylene | 0.10 (0.53) | 2.9 (6.86) | 4.43 (8.54) | 7.22 (12.49) |
| propane | 0.40 (2.13) | 3.1 (7.33) | 5.37 (10.35) | 4.71 (8.15) |
| propene | 0.10 (0.53) | 2.6 (6.15) | 3.01 (5.80) | 3.66 (6.33) |
| $C_4$ $(i+n)$ | – – | 0.6 (1.42) | 1.80 (3.47) | 1.56 (2.70) |
| $\sum C_4$ unsat. | 0.10 (0.53) | 2.5 (5.91) | 2.54 (4.89) | 2.78 (4.81) |
| $n$-$C_5$ | – – | 0.10 (0.24) | 0.15 (0.29) | 0.09 (0.16) |
| cyclopentene | – – | 1.10 (2.60) | 1.49 (2.87) | 1.49 (2.58) |
| octene[b] | – – | 1.30 (3.07) | 1.38 (2.66) | 1.38 (2.39) |
| total amount | 18.8 | 42.3 | 51.9 | 57.8 |

[a] The quantities are expressed in $10^{-8}$ mol of the equivalent amounts of $CH_4$. Numbers in parentheses indicate the selectivity (%) of the homologated $CH_4$ into the respective hydrocarbon. Experimental conditions: exposure to $CH_4$ (30 s, 110 $cm^3$/min) followed by a dose of 1.4 $cm^3$ (ambient pressure) of (He, $x$% CO).

[b] Unidentified octene.

plementary effect and prolongation of the CO feed for 1 min does not entail any appreciable further increase of the quantity of every product.

It is worthwhile mentioning that if the dose of CO is sent to the *clean* catalyst (no previous exposure to $CH_4$) only $CH_4$ is formed upon the subsequent hydrogenation. Moreover, fig. 2 shows the spectrum of temperature programmed surface reaction with $H_2$ (TPSR) of CO preadsorbed at 250°C. From it, one can deduce that only part of the CO adlayer can be reacted off within a few minutes at 250°C since more than 25 min beyond attainment of 250°C are required during programmed heating for completing the reaction.

## 4. Discussion

It is well known that Pt is unable to convert $CO/H_2$ mixtures to hydrocarbons higher than $CH_4$, which has been checked by using our catalyst as well by cofeeding it with both reactants as by hydrogenating pre-adsorbed CO. This strongly suggests that fast and total hydrogenation of the carbon takes place upon the breaking of the CO bond with immediate release of methane. No C–C bond formation can therefore occur since no $CH_x$ species can build up on the surface. Deeply different is the situation prevailing during exposure to $CH_4$, since $CH_3$ species are allowed to cover the surface where they can loose hydrogen because of the parallel $H_2$ desorption. C–C bonding processes can reasonably be imagined between near H-deficient $CH_x$ species adsorbed on suitable metals and this turns out to be the

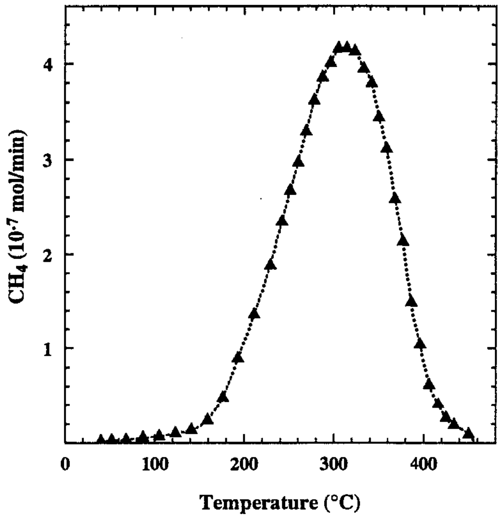

Fig. 2. Temperature programmed surface reaction with hydrogen of pre-adsorbed CO. Experimental conditions: adsorption: a dose of 1.4 $cm^3$ (ambient pressure) of CO pre-adsorbed at 250°C; TPSR: under a flow (50 $cm^3$/min) of $H_2$ with a temperature ramp of 6 K/min.

case on platinum as on other metals [2]. Further supply of $H_2$ removes the $C_{2+}$ precursors as higher alkanes despite the fact that some of them undergo hydrogenolysis.

In contrast with platinum, true Fischer–Tropsch catalysts allow the building-up of various hydrocarbonaceous species on their surfaces. From the preceding view, one can deduce that if $H_2$ was present during chemisorption of $CH_4$ on such catalysts higher hydrocarbons could be obtained in a continuous mode. Not only in that case would the chemisorption of $CH_4$ be severely inhibited by $H_2$ but no $H_2$ would be removed from the methyl species which would result from the few $CH_4$ molecules that would succeed in bonding to the surface. That conclusion is nothing else than the kinetic translation of the severe thermodynamic constraint to which the $CH_4$ homologation is opposed.

No spontaneous desorption of any hydrocarbon other than $CH_4$ occurs when a flow of He is substituted for that of $CH_4$ at the end of the exposure of the Pt to $CH_4$. Therefrom we deduce that the release of numerous alkanes and alkenes (20 to 30 according to the conditions) when the metal receives a dose of CO after preliminary adsorption of $CH_4$, does not result from the mere disappearance of $CH_4$ from the gaseous phase. As no oxygenates are present among the products, we are led to conclude that not only does CO chemisorb on the sites of Pt remaining available but, also, it can push aside hydrocarbonaceous adspecies and substitute for them on the surface. As a first interpretation, we may assume that the major part of the released species simply results from this induced desorption. However, alkanes (or hydrocarbons more generally) are not chemisorbed as such and their surface precursors, more or less H-deficient, need some hydrogen before turning into the corresponding free molecules. Associative desorption involving near $C_xH_{2x+1}$ and H adspecies is therefore expected to take place and explains alkane formation, according to:

$$\mathrm{CO} + \underset{*}{\mathrm{H}} + \underset{*}{\mathrm{C}}_x\mathrm{H}_{2x+1} \rightarrow \underset{**}{\mathrm{CO}} + \mathrm{C}_x\mathrm{H}_{2x+2}\,.$$

One cannot exclude either that coupling of two carbonaceous adspecies may happen upon their associative desorption as in the following possible reaction:

$$\mathrm{CO} + \underset{**}{\mathrm{CH}_2} + \underset{**}{\mathrm{CH}_2} \rightarrow \underset{**}{\mathrm{CO}} + \mathrm{C}_2\mathrm{H}_4\,.$$

Although chain-lengthening due to alkyl-coupling through associative desorption of precursors possessing several carbon atoms may be imagined, such a process remains little probable in view of the fact that the heaviest hydrocarbons removed by CO are not much longer than those removed by $H_2$, and this is so despite some possible chain shortening due to hydrogenolysis in the latter case.

In addition we must also remark that not all the $C_xH_y$ adspecies can be dislodged by CO due to their possible too great H-deficiency which excludes their existence as free molecules.

We can therefore conclude that numerous hydrocarbonaceous adspecies are formed on the surface of Pt upon mere exposure to $CH_4$ at moderate temperatures.

To our knowledge, Ceyer et al. were the first to demonstrate, by using molecular beam techniques and high-resolution electron energy loss spectroscopy, that C–C bond formation could occur on Ni(111) between CH adspecies resulting from collision-induced dissociative chemisorption at 47 K followed by adequate heating which caused $CH_3$ dissociation and $H_2$ desorption [5]. Recently, Goodman et al. have evidenced ethylidyne and vinylidene on Ru($11\bar{2}0$) after adsorption of $CH_4$ at 120–420°C and at a pressure of 5 Torr. However, no formation of $C_{3+}$ precursors could be evidenced [6]. Apart from those two contributions no other evidence of C–C bonding upon chemisorption of $CH_4$ on metals emerged from so many surface science studies carried out on single crystals. As recently suggested, the reason for that failure might well be found in the excessive dehydrogenation of the $CH_x$ adspecies, which would be induced by the vanishingly low $H_2$ pressure prevailing in ultra-high vacuum conditions [7].

Extensive dehydrogenation leading to pure carbon deposits may also take place on usual catalysts contacted with $CH_4$ at temperatures allowing complete decomposition of $CH_4$ to proceed [8]. As argued by van Santen et al. different kinds of carbon deposits are then formed and reaction of some of them with $H_2$ at a much lower temperature may lead to alkanes ranging from $C_1$ to $C_5$ as was observed by Rabo et al. in the case of CO disproportionation on Ni, Ru and Co [9]. However our present report contributes to show that contacting suitable metal surfaces with methane at moderate temperatures can lead to a much wealthier chemistry than mere carbon deposits.

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