LETTER TO THE EDITOR

Does C–C Bonding Proceed during Exposure of Adequate Metal Surfaces to CH₄? Reply to "Comment by Z. Hlavathy, Z. Paál, and P. Tétényi"

The comments, results, and reflections presented by Hlavathy and co-workers in their Letter aim at demonstrating that C–C bonding between CH_x adspecies, formed upon exposure of Pt to CH_4, can proceed as well during the exposure itself as during further exposure to H_2.

This possibility was implicitly put forward by Koerts *et al.* (1) because they thought that a tight parallelism exists between the interactions of CH_4 and CO with a metal surface, provided that the exposure to CH_4 is carried out at a high enough temperature (450°C). In both cases these authors assumed that three kinds of carbon, C_α, C_β, and C_γ, can be formed, C_α being the main species responsible for the production of CH_4 and of the C_{2+} alkanes obtained when the metal was further contacted with H_2 at 100°C. As they argued that C_α (also named carbidic carbon) has only metal atoms in its first coordination shell, they were implicitly led to admit that C–C bonding must take place during the hydrogenation step.

In our contributions (2, 3) (as well as in preceding reports), we have not denied this possibility but we have suggested that different situations can result from exposures to CH_4 conducted at temperatures much lower than those having prevailed in the experiments reported by Koerts *et al.* We do not see why C–C bonding could not proceed between *close* and sufficiently H-deficient CH_x adspecies. We have therefore proposed that the precursors of higher hydrocarbons (that is, adspecies containing at least the same number of C atoms as the corresponding hydrocarbons released upon further admission of H_2) are reasonably formed on the surface during the first step. In support of this view additional arguments will be given in future contributions but we have already reported that, after exposure of EUROPT-1 to CH_4 under our conditions, supplying the catalyst with CO instead of H_2 removed a number of hydrocarbons ranging up to C_8, among which a good part were olefins (4). No oxygenates appeared and the role of CO was therefore only to dislodge part of the removable adspecies which would have been completely hydrogenated in H_2.

The authors of the preceding Letter argue that the possibility of C–C bonding upon mere adsorption of methane on a Pt foil, in the absence of hydrogen, is demonstrated by the evolution of ethane during the adsorption. We have

also reported the same observation, although it was obtained under different conditions and with a supported Pt sample instead of bulk Pt. However, we do not find there sure evidence for the existence of a C_2 species on the surface because this species might have been formed through an associative desorption process just as, for instance, H_2 is formed upon desorption from platinum, no H–H species existing on the surface. Evolution of some propane, observed in their experiments at 150 and 200°C during the step that they call "evacuation," provides more convincing evidence for the formation of C–C bonds during the mere exposure to CH_4, due to the very slight probability of an associative desorption involving three adspecies simultaneously.

When comparing their results with ours, Hlavathy and co-workers do not comment on the possible effect of the very large difference of pressures (six orders of magnitude) existing between both series of experiments and concerning CH_4 as well as H_2. All our experience has convinced us that very different situations can arise depending upon the specific conditions of exposure of the catalyst to CH_4. The true composition of the resulting adlayer, and therefore of the C_{2+} products removed in the second step, is highly dependent upon the latter conditions.

In order to better appreciate the preceding statement, we have to imagine what may take place when the metal is contacted with CH_4. True decomposition of methane, as represented by

$$CH_4 \rightleftarrows C + 2\,H_2,$$
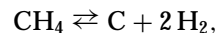
where C stands for *bulk* carbon, is obviously favored at increasing temperatures. At equilibrium the fraction of decomposed methane is a decreasing function of the pressure. At low enough temperatures, only dissociative adsorption giving rise to adsorbed CH_3 and H can proceed, while heating can allow hydrogen desorption to parallel the chemisorption process and accordingly further loss of hydrogen to be undergone by the carbonaceous adspecies. Therefore, at intermediate temperatures, we must consider simultaneous occurrences of several interfering processes. The question which we now must raise is whether C–C bondings between CH_x adspecies have to be considered as possible additional processes. If only adsorbed

methyls were present on the surface, no C–C bonding could take place but desorption of hydrogen makes further loss of hydrogen possible, resulting in the formation of H-deficient adspecies between which C–C bonding becomes expectable, on adequate metal surfaces at least. Such an expectation is quite in line with the reverse common acceptance that the C–C bond present in C_2H_4 does not break easily upon chemisorption. We have already shown that preliminary chemisorption of ethylene on EUROPT-1 followed by hydrogenation can lead to the formation of C_{3+} hydrocarbons among which those containing an *even* number of C atoms are largely prevailing (5). We will soon report similar results concerning the case of ethane. These observations are a clear indication that the most abundant building units contain a C–C bond and most probably are the chemisorbed ethylene molecules themselves. Infrared spectroscopic evidence for that has been reported (6, 7). Why not reversely imagine therefore that two neighbor CH_2 adspecies can react and generate adsorbed ethylene? Further bonding can equally well proceed and this is illustrated by another known example which is the trimerization of adsorbed acetylene into benzene on various surfaces (8).

HREELS evidence for C–C bond formation upon adsorption of methane on single crystal surfaces of Ru has been reported by Wu and Goodman (9) but the most interesting and remarkable demonstration was that reported by Yang *et al.* a few years earlier in the case of Ni(111) (10). The latter authors, also using HREELS and molecular beam facilities, succeeded in showing the successive formations of CH_3, CH, C_2H_2, and C_6H_6 at the surface, followed by thermal desorption of benzene.

From this we conclude that there exists a *continuum of situations* between mere chemisorption (no H_2 desorption at all) and true decomposition of methane on metal surfaces. What actually results from a given exposure is expected to tightly depend upon the specific conditions, including not only temperature and pressure but also *the way according to which the exposure is carried out* since, in almost all cases, H_2 evolution proceeds during exposure and CH_4 does not remain pure. For instance, in a plug-flow reactor the flow rate becomes a significant factor (2, 3) and, what is commonly ignored in experiments involving a sample of small area (single crystal or piece of bulk metal) statically exposed to CH_4, the reactor volume does the same since the evolved H_2 expands into it and establishes its pressure at a level directly depending upon the volume and significantly contributing to the determination of the H-deficiency of the carbonaceous adspecies.

In their experiments, Koerts *et al.* (1) exposed their catalysts to CH_4 diluted into He and at more than 400°C. Low methane pressure and high temperature favor the formation of C_γ although they do not prevent that of some reactive carbon leading to the release of methane and some C_{2+} products (mainly ethane and propane) during subsequent hydrogenation, provided sufficient cooling is applied before it. The best results were obtained at low coverages, which is surprising because chain lengthening should be enhanced by the closeness of C atoms resulting from increasing coverages. However, exposures leading to limited coverages also lead to less C_γ formed from reactive carbon, so that the correspondingly improved results do not necessarily mean that the C atoms must remain isolated in order that the probability of their further conversion into higher alkanes be increased. The existence of C–C bonds in reactive carbon deposits, even excluding the presence of hydrogen, remains a debatable question. In effect, Hutson *et al.* (11) recognized the presence of significant amounts of C–C bonds on Ni(100) and Ni(111) contacted with CO and mentioned the existence of adspecies such as C_2, C_3, and so on. . . . Moreover, reviewing the results obtained when the Fischer–Tropsch synthesis is carried out under periodical feeding of the catalyst with CO or H_2, Adesina *et al.* were led to conclude that "chain growth does not occur during the H_2-pulse portion of a cycle" (12).

It may also be worthwhile here to recall that in a very different kind of reaction, namely that of ionic carbides with water or dilute acids, the length of the resulting hydrocarbon (methane, acetylene, methyl-acetylene) is dictated by the number of the C atoms bonded to one another in the bulk carbide and not by what happens when the carbide is contacted with the hydrogenating agent (13).

Must we, however, dismiss the possibility that H_2 may help C–C bonding to proceed? Starting from CH_4, no chain lengthening can proceed without release of H_2 but we can assume that total dehydrogenation may not be kinetically favorable. Excessive dehydrogenation can lead to the formation of elemental C atoms, triply bonded to the surface and with a restricted mobility. Limited supply of H_2 may be expected to enhance the adspecies mobility and so to favor the C–C bonding processes. Despite this possible positive effect of H_2, we also must take into account a countereffect due to H_2, i.e., hydrogenolysis. The supply of H_2 at high temperature will break most of the higher alkanes into methane. This is why Koerts *et al.*, after having decomposed CH_4 at a relatively high temperature (450°C), were led to the practice of strongly cooling the metal before supplying H_2. Nevertheless, even at 100°C, the hydrogenation of reactive carbon into CH_4 strongly competes with the formation of C_{2+} products.

Our experience strongly prompts us to think that, if hydrogen removal is obviously necessary in order to convert methane into higher alkanes, it is inappropriate to remove the hydrogen completely and to revert to carbon, even "carbidic." On the contrary, *adequate hydrogen removal* may lead, during exposure of the catalyst to methane, to a surface chemistry of great wealth and to the whole hydrocarbon chemistry compatible with the nature of the metal used. As moderate temperatures are to be used for reaching

good composition of the adlayer, isothermal operation becomes possible and even some hydrogenolysis in the second step may bring a positive contribution since, at high coverages, too heavy precursors may not be released as such and may need to be cut into lighter fragments before leaving the surface. We will give evidence for that in forthcoming reports.

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