

LETTER TO THE EDITOR

Comment on “Oxygen-Free Conversion of Methane to Higher Alkanes through an Isothermal Two-Step Reaction on Platinum (EUROPT-1)” by Mohamed Belgued, Annie Amariglio, Pierre Paréja, and Henri Amariglio

The Nancy Catalysis Group reported in a recently published series (1, 2) on the conversion of methane to ethane and higher hydrocarbons over Pt/Al₂O₃ at comparatively low temperatures, $T \geq 150^\circ\text{C}$. As they suggested, the conversion occurred in two steps:

1. adsorption of CH₄ on Pt with formation of H-deficient CH_x fragments and of C–C bonds between them;
2. desorption of C₂-species and those of higher carbon number upon hydrogenation.

The authors found an optimum temperature for methane homologation (250°C). The temperature of homologation is determined by the temperature of the adsorption of CH₄ from one side and by the temperature of the opposite reaction, i.e., hydrogenolysis of C–C bonds, from the other.

These statements are in agreement with the authors' previous communications with respect to this reaction on Pt (3, 4) and with the contribution of Koerts and van Santen, reporting on two-step homologation of methane on Co, Ru, and Rh (5). There exists, however, a certain difference between them in the understanding of the two steps: the Nancy group assumes that C–C bond formation takes place between H-deficient CH_x fragments during the chemisorption step, whereas van Santen and his colleagues are of the opinion that the carbonaceous intermediates produce small alkanes upon hydrogenation.

The observations of both teams are in agreement, however, with respect to the process controlling role of the methane adsorption: the production of ethane and higher hydrocarbons becomes possible at temperatures where methane chemisorption commences.

In an earlier communication (6) we reported on the adsorption of alkanes on Pt ribbon as measured by work function changes. Pt (cleaned by flashing up to 1250 K and by subsequent Ar⁺ ion sputtering) adsorbed methane (10⁻³ mbar) at temperatures between 50 and 300°C. The adsorption was highly irreversible: 10–20% of methane only was desorbed *in vacuo*. Hydrogen added to the system swept out more than 30% of methane at 50°C. (No desorption with hydrogen was observed at tem-

peratures higher than 150°C.) Similar observations were made with ethane, propane, and neopentane. The adsorption of methane at low temperatures and the formation of hydrogen-deficient adspecies—evidenced by the hydrogenative desorption—also suggests the possibility of C–C bond formation. It is of interest therefore to determine the chemical composition of hydrocarbons desorbed from Pt after its exposure to methane *in vacuo* and by hydrogen. This could answer the following questions:

- (i) whether C–C bond formation occurs at temperatures lower than 150°C since CH₄-adsorption takes place at these temperatures;
- (ii) whether the effect of hydrogen is limited to desorption of hydrogen-deficient C–C adspecies formed during the chemisorption step, or whether it plays a specific role also in the production of C₂-species (e.g., by hydrogenation of the surface carbonaceous intermediates).

With the aim of determining the chemical composition of gases desorbed from the Pt foil, the apparatus for work function change measurements, described in details elsewhere (6), was equipped with a Balzers QMG 420 quadrupole mass spectrometer (QMS). The schematic representation of the apparatus is given (Fig. 1).

After the Pt foil was exposed to methane (10⁻³ mbar) for 10 min in an isolation chamber, the gas was admitted to the QMS in order to determine its chemical composition, i.e., the degree of its conversion (procedure “a”). The chamber was then evacuated (to 10⁻⁸ mbar), the sample was treated *in vacuo* for 10 min (procedure “e”), and the contents of the chamber were admitted to the QMS. The sample was then exposed to 5×10^{-4} mbar of hydrogen for 6 min and the composition of the outflow gases was determined (procedure “h”).

Corrections were made in cases when it was necessary for the “background effect” (composition of the outflow gases in case of totally deactivated Pt) and for the CO–hydrocarbon conversion determined by special measurements.

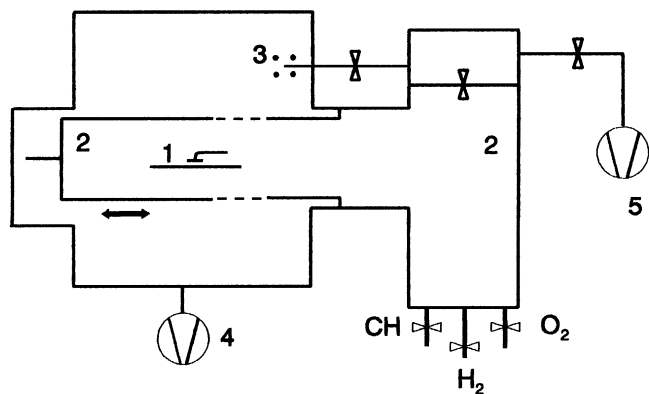


FIG. 1. Schematic diagram of the apparatus setup: 1. Pt foil. 2. Isolation chamber. 3. QMS. 4. Ion pump. 5. Oil diffusion pump.

Figure 2a gives the distribution of hydrocarbons in the outflow gases obtained from the different procedures. The conversion of methane (procedure "a") was only 1–2% at low and 3–4% at higher temperatures (4% conversion corresponded to TOF: $9.76 \times 10^{-4} \text{ s}^{-1}$). The distribution of hydrocarbons desorbed *in vacuo* (procedure "e") indicated that a significant ratio of methane was transformed to ethane. It follows from this that—in agreement with suggestion made by Belgued *et al.* (2)—both the formation of CH_x adspecies and C–C bonding between them take place during the chemisorption step.

Mass spectra obtained after hydrogenative treatment following evacuation indicated the presence of hydrocarbons in the outflow gases, in agreement with the observation of Garin *et al.* (7). The ratio of C_2 hydrocarbons was, however, higher in gases desorbed by hydrogenative treatment (procedure "h") than that obtained *in vacuo*. This indicates that hydrogen produced ethane in part by hydrogenation of carbonaceous intermediates (deposits) in accordance with a suggestion made by van Santen's group (5). The bond formation upon low-temperature adsorption supports the conclusion of Belgued *et al.* on the decisive (controlling) role of CH_4 adsorption in the conversion of methane to higher alkanes.

The ratio of ethane produced from methane was highest at 200°C , both by treatment *in vacuo* and in H_2 . It decreased at $T > 200^\circ\text{C}$, which was caused presumably by C–C bond scission. This is well seen from data on distribution of hydrocarbons obtained at adsorption and subsequent treatment of ethane (Fig. 2b). A low but noticeable conversion of ethane (TOF = $2.4 \times 10^{-3} \text{ s}^{-1}$) takes place on Pt (procedure "a"). In this respect, ethane—in agreement with earlier observations (8)—is more reactive than methane. C–C bond formation (production of C_3) is observed at low temperatures, but the ratio of C_3 products is substantially lower than that of C_2 from methane (TOF = $7.3 \times 10^{-4} \text{ s}^{-1}$ at 200°C). It is noticeable that the ratio of methane produced from ethane is higher in products desorbed *in vacuo* at all tem-

peratures than that produced upon treatment in hydrogen. This indicates that a high ratio of C–C bonds is broken at chemisorption and mostly CH_x adspecies are formed on the surface. In excess of hydrogen, C_2 species are formed due to interaction with irreversibly adsorbed surface intermediates. At temperatures higher than 200°C , C_1 formation prevails in hydrogen excess also.

The low ratio of production of C_3 hydrocarbons following ethane adsorption (as compared to ethane formation from methane) can be attributed to two reasons. First, the reverse reaction, i.e., propane hydrogenolysis, is substantially higher than that of ethane (8). The conversion of propane to $\text{C}_1 + \text{C}_2$ on our Pt ribbon (procedure "a") was 8–21% at different temperatures (TOF = $6.2 \times 10^{-3} \text{ s}^{-1}$ at 200°C). The abundance of $\text{C}_1 + \text{C}_2$ among the hydrocarbons desorbed *in vacuo* was 64–89%, whereas this value reached 85–100% in the outflow gas after H_2 treatment. The elevated reactivity of propane was explained (9) by π -allyl adsorption of C_3 hydrocarbons prior to hydrogenolysis, which is impossible with ethane. On the other hand, the mechanism of chain lengthening may also change from methane to ethane. The C_2 feed opens up the pathway involving carbene–alkene

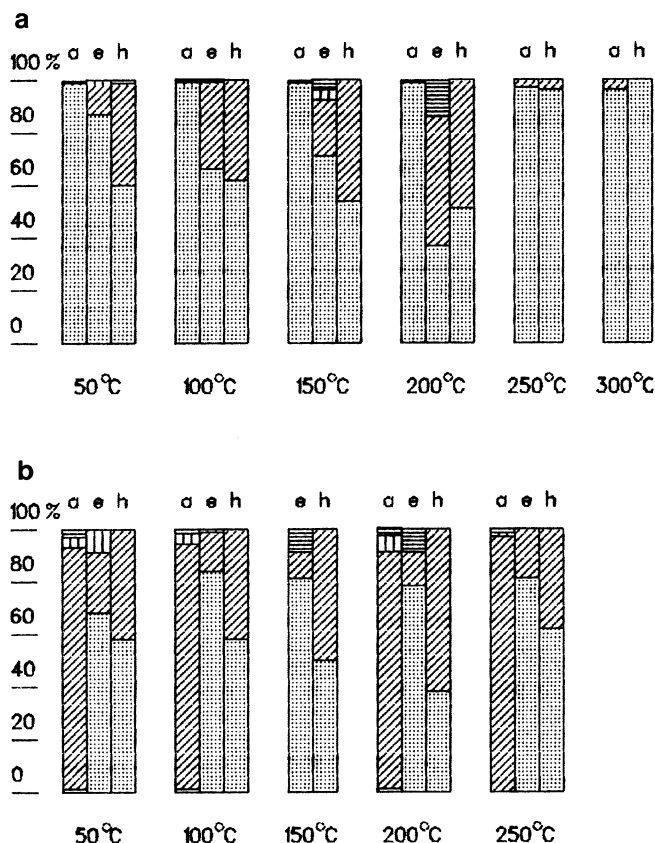


FIG. 2. Distribution of hydrocarbons, obtained on Pt foil at various temperatures from methane (a) and ethane (b). Procedures: a. after exposure to methane; e. after evacuation; h. after H_2 -treatment, subsequent to evacuation. (□) CH_4 ; (▨) C_2H_6 ; (▩) C_2H_4 ; (▮) C_3H_8 .

insertion (10, 11). This, however, requires higher temperatures and hydrogen-deficient conditions (11).

We found the threshold temperature of ethane formation from methane to be significantly lower on Pt ribbon surface than over EUROPT-1. Two possible reasons can be given for this. One is the higher propensity of clean Pt foil to adsorb methane as the foil exposes more contiguous metal active sites than the EUROPT-1 of rather high dispersion. The other is the migration ability of dehydrogenated CH_x ad-species to the support on EUROPT-1. This possibility was demonstrated on various supported Pt and could lead to accumulation of carbonaceous entities on the metal-support interface (12). Similar considerations were proposed by Koerts *et al.* No such reaction is possible on a Pt ribbon.

To summarize, we believe that C-C bond formation from methane takes place both during the chemisorption process and as a result of hydrogen interaction with adsorbed CH_x entities on the Pt surface. The optimum temperature for this reaction was found to be 150–200°C, which is lower than that reported by Belgued *et al.* (2) with EUROPT-1 and much lower than step 1 proposed by Koerts *et al.* (5) on various transition metals. However, our temperature range agrees quite well with their proposed step 2 (desorption step). Hence Pt foil seems to be able to dissociate methane at lower temperature, so the second step, the hydrogenative desorption, becomes possible.

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Z. Hlavathy¹
Z. Paál
P. Tétényi

*Institute of Isotopes
Hungarian Academy of Science
P.O. Box 77
Budapest, H-1525, Hungary*

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¹ E-mail: hlvathy@iserv.iki.kfki.hu.