

Possibility of obtaining Appreciable Yields in Methane Homologation through a Two-step Reaction at 250°C on a Platinum Catalyst

Annie Amariglio, Pierre Paréja, Mohammed Belgued and Henri Amariglio*

Laboratoire de Catalyse Hétérogène, Université de Nancy I, BP 239, 54506 Vandœuvre les Nancy, France

Methane is converted (>40% yield) to higher alkanes at 250°C on exposure to a Pt/SiO₂ catalyst and subsequent treatment with hydrogen.

It has recently been reported that metal-supported catalysts can be used in a two-step reaction sequence for homologating methane.¹⁻⁷ In the first step, methane is chemisorbed^{1,3,4} or decomposed^{2,5-7} on the metal and in the second step the resulting species are submitted to a flux of hydrogen. The reaction of hydrogen with the surface species can proceed either at the same temperature as the first step^{1,3,4,7} or at a lower one.^{2,4-6}

Our previous, modest^{1,3,4} yields of C₂₊ alkanes can be explained by the double role of the flow of methane used in the first step. Methane not only behaves as a reactant but also acts as a carrier gas conveying the desorbed hydrogen out of the reactor. The removal of hydrogen by the flow of methane is a most important feature of the procedure under study since it allows more CH_x species to concentrate on the surface and also governs their H-deficiency and therefore their ability to bond with one another.

To increase the yield on the basis of the consumed methane, less methane should be used and hydrogen continuously removed. Here, we describe results obtained using a batch reactor with a limited amount of methane. The amount of methane chemisorbed on the metal could be calculated from the pressure lowering caused by adsorption.

The catalyst consisted of 1 g of Europt-18 contained in a quartz reactor (6.7 ml) and activated as previously described.^{1,3} The reactor could be made part of either a methane circuit (step 1) or a hydrogen circuit (step 2). The methane circuit contained a recirculating pump, a palladium catalyst at room temp. used as a hydrogen trap (5 g of a 5 wt% Pd/Al₂O₃ catalyst; Johnson-Matthey, type 24 A, No. 524 A/42) and the sampling loop of a first chromatograph. Its total volume was nearly 40 ml and the pressure could be measured with a piezometric transducer allowing pressure variations as low as 1 mbar to be easily measured. The methane was furnished by Air Liquide and did not contain any detectable C₂₊ (<0.1 ppm). No further purification was used in order not to increase the volume of the methane reservoir. The initial pressure of methane was 1 bar. The hydrogen circuit contained a trap filled with glass beads, cooled in a bath of liquid air and aimed at collecting the C₂₊ products. At the end of the second step the hydrocarbon trap was made part of a third closed circuit including a recirculating pump and the sampling loop of a second chromatograph.

Initial filling up of the circuit with methane was done while maintaining the catalyst at room temp. whereupon the catalyst was heated at the desired temperature. The gas was maintained immobile during the heating, so that the hydrogen evolved owing to the chemisorption occurring during this ill-defined transient period hindered the chemisorption. Recirculation started as soon as the desired temperature was reached, which took a few minutes. After exposure, the reactor was switched from the methane circuit to the hydrogen one, the pressure of the methane circuit was measured and methane was analysed as regards hydrogen and ethane evolved from the catalyst.

Table 1 displays the result of a 16 min exposure to methane at 250°C, followed by hydrogenation at the same temperature. 27 chromatographically separated alkanes were obtained, among which C₅–C₈ alkanes represented more than 59% of the converted methane. The total C₂₊ production was equivalent to 24.6 μmol of CH₄. The corresponding pressure

decrease in the methane reservoir after exposure was equal to 39 mbar, which corresponded to 63.2 μmol, so that the yield to C₂₊ with respect to the consumed methane was 38.9%. In addition to this production of higher alkanes during the hydrogenation step, some ethane was produced during the exposure as already reported.¹ Analysis of the gas contained in the methane reservoir gave a C₂ concentration of 845 ppm, corresponding to 1.40 μmol of ethane. This amount of ethane was not lost since it could be involved in a second run in which part could give rise to further homologation, the remainder being unchanged or reverted to methane.⁹

Not all the ethane produced during the first step was present in the gas. We could demonstrate in a separate experiment that in the pressure range concerned some ethane was adsorbed on the palladium sample used as a hydrogen trap. We also checked that this ethane could be dislodged by hydrogen, even at the low pressure at which hydrogen is formed during the first step, because hydrogen is irreversibly chemisorbed. Accordingly, it was not lost either.

Taking all that into account allows us to state that the yield expressed on the basis of the methane removed from the batch reactor amounted to 42.5% at a conservative estimate. This yield is not expressed on the basis of the total amount of methane contained in the circuit (which may be considered as an initial investment) but on that of the amount of methane which had to be added into the circuit at the end of each cycle in order to carry out the following one under identical conditions. The remaining 57.5% represented the methane

Table 1 Quantity of C₂₊ alkanes resulting from a 16 min exposure to methane at 250°C and subsequent hydrogenation

Alkane			Quantity/μmol
C ₂			3.56
C ₃			0.64
Σ C ₄			0.242
	<i>iso</i> -C ₄	0.030	
	<i>n</i> -C ₄	0.212	
Σ C ₅			1.334
	<i>c</i> -C ₅	0.545	
	<i>iso</i> -C ₅	0.029	
	<i>n</i> -C ₅	0.760	
Σ C ₆			1.092
	<i>c</i> -C ₆	0.353	
	Methyl- <i>c</i> -C ₅	0.289	
	2-Methyl C ₅		
	+	0.311	
	3-Methyl C ₅		
	<i>n</i> -C ₆	0.139	
Σ C ₇			0.171
	Methyl- <i>c</i> -C ₆	0.0125	
	Unidentified C ₇	0.0260	
	3-Methyl C ₆	0.0116	
	2-Methyl C ₆	0.0087	
	2,3 Dimethyl C ₅	0.0434	
	2,4 Dimethyl C ₅	0.0280	
	<i>n</i> -C ₇	0.0405	
Σ C ₈			0.023
	Total amount of homologated CH ₄		
	24.6 ^a		

^a 14.7 at 5 min exposure, 9.34 at 1 min exposure.

into which the corresponding amount of chemisorbed species was back reacted and which was mixed up with the products of the second step.

In another experiment, the catalyst was submitted again to methane under the same conditions as previously. This exposure was followed first by a temperature-programmed desorption (TPD) in flowing argon, second by a temperature-programmed reaction with hydrogen (TPSR) in order to react the carbonaceous residues remaining on the surface. In TPD as well as in TPSR, methane was by far the main product. The amount of adsorbed methane so determined was in good agreement with that deduced from measurement of the pressure decrease.

Repetition of the two-step reaction in conditions equal to that leading to the results displayed in Table 1 but without the Pd trap showed that after exposure the methane contained 51

ppm ethane (instead of 845 ppm) and 1500 ppm H_2 (instead of traces previously). The production of each C_{2+} was strongly lowered by a factor increasing from 2.6 for C_2 to 7.7 for $n-C_6$ whereas only traces of C_{7+} were detected.

Shorter exposures were also studied at the same temperature but without pressure measurements as they would have lacked accuracy, see footnote to Table 1. One can see that the influence of the exposure duration on the total amount of homologated methane is relatively small as dividing the exposure duration by a factor of 16 resulted in the division of the amount of homologated methane by 2.5 only. The main differences concerned the distribution of the products as exemplified by Fig. 1. For the 5 min exposure as well as for the 1 min one, only traces of C_7 and C_8 were observable, C_{4+} were lower than in the case of the 16 min exposure and C_2-C_4 were the most abundant alkanes. This clearly shows that increasing the duration of the exposure favours the higher alkanes.

This work was supported by Gaz de France. We thank J. Saint-Just for fruitful discussions.

Received, 8th November 1993; Com. 3/06683E

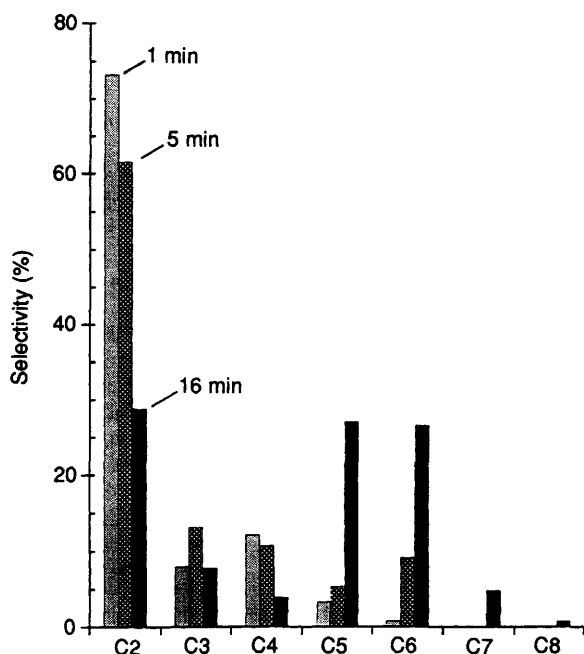


Fig. 1 Variation of the distribution of the C_{2+} alkanes vs. the duration of the exposure to methane ($T = 250^\circ C$)

References

- 1 M. Belgued, P. Paréja, A. Amariglio and H. Amariglio, *Nature*, 1991, **352**, 789.
- 2 T. Koerts and R. A. van Santen, *J. Chem. Soc., Chem. Commun.*, 1991, 1281.
- 3 M. Belgued, H. Amariglio, P. Paréja, A. Amariglio and J. Saint-Just, *Catal. Today*, 1992, **13**, 437.
- 4 M. Belgued, S. Monteverdi, P. Paréja, H. Amariglio, A. Amariglio and J. Saint-Just, *Prepr. Symp. Natural Gas Upgrading II*, Div. of Petrol. Chem., Inc. Am. Chem. Soc., San Francisco, CA., 5–10 April 1992, 1992, **37(1)**, 324.
- 5 T. Koerts and R. A. van Santen, *Prepr. Symp. Natural Gas Upgrading II*, Div. of Petrol. Chem., Inc. Am. Chem. Soc., San Francisco, CA., 5–10 April 1992, 1992, **37(1)**, 336.
- 6 T. Koerts, M. J. A. G. Deelen and R. A. van Santen, *J. Catal.*, 1992, **138**, 101.
- 7 F. Solymosi, A. Erdöhelyi and J. Cserényi, *Cat. Lett.*, 1992, **16**, 399.
- 8 G. C. Bond and Z. Paál, *Appl. Cat. A*, 1992, **86**, 1.
- 9 A. Amariglio, L. Lefort, M. Belgued and H. Amariglio, *Prepr. Europacat-1*, Montpellier, France, 12–17 September 1993, 1993, **2**, 564.