Low temperature selective methane activation to alkenes by a new hydrogen-accumulating system

M. V. Tsodikov,[a] Ye. V. Slivinskii,[a] V. P. Mordovin,[a] O. V. Bukhtenko,[a] G. Colón,[b] M. C. Hidalgo[b] and J. A. Navío*[b]

[a] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 117912-Moscow, Leninskii prosp. 29, Russia*

[b] *Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla and Dpto. de Química Inorgánica, Universidad de Sevilla, Avda. Américo Vespucio, s/n. 41092-Sevilla, Spain. E-mail: navio@cica.es*

Received (in Cambridge, UK) 22nd February 1999, Accepted 16th April 1999

A heterogeneous hydrogen-accumulating system containing porous titanium with 0.4 wt% Ni combined with high-purity titanium chips was tested for methane activation; methane conversion to C_1–C_4 hydrocarbons reached a value of *ca.* 20% over this material, working at 450 °C and 10 atm, after methane circulation across the system for 22 h; the split hydrogen was accumulated as TiH_2, being in solid solution with porous metallic titanium.

Methane is the principal constituent of natural gas, landfill gas or coalbed methane. It is also a by-product of oil refining and chemical processing. Many techniques have been developed for improving the industrial processes which convert methane into higher hydrocarbons, gasoline and olefins by both indirect and direct conversion processes.[1,2] However these industrial processes involve expensive separation steps and/or require the use of temperatures higher than 80 °C, with the subsequent consumption of energy.[1,2]

Direct methane conversion eliminates the need (and subsequently reduces the cost) for the syngas preparation step. However, since methane is a very stable molecule[2,3] its reactions generally have high activation energy and, once activated, it is difficult to stop the reaction from going further than desired.

On the other hand, the non-favourable thermodynamic parameters[4] for methane self-interaction reactions led us to predict that, without strong oxidants, it would be difficult to transform methane into higher homologues at moderate temperatures using conventional catalytic approaches. We presumed, however, that it should be possible to shift the equilibrium *via* the introduction of separate stages, including the formation of [CH_3*] and [CH_2*] intermediates using heterogeneous systems with dual activities: a high activity for C–H bond fission and simultaneous hydrogen-accumulating properties. The latter might lead to an increase in the probability of direct self-interactions between generated intermediates, giving higher hydrocarbon molecules by a route which has not been explored until now. The adsorption of H_2 on transition metals has been much studied.[5] At the same time the adsorption/reaction of hydrocarbons on metallic catalysts is a very well known topic,[5] with Ni metal having a capability for hydrogenolysis of C–C and steam reforming of CH_4.

With this goal in mind we used a heterogeneous system containing porous high purity titanium (99.6%) with 0.4 wt% Ni in the form of cylindrical pellets (10 mm long and 5 mm in diameter) (**I**) combined with titanium chips (**II**) also obtained from high purity titanium. The **I**:**II** ratio was 5.3. The composite was thermally activated at 850 °C *in vacuo* (10^{-5} torr) before being placed in a loop reactor with a total volume of 0.42 L in circulation mode with a flow rate of 5 L of gas per hour at 10 atm. It was shown by laser (ML-2) and scanning high temperature mass spectroscopy (VIMS MS-720) that vacuum treatment is sufficient to clean up the surface. Using 19 g of this catalytic material it was found that methane conversion reached around 20% after methane flow-circulation across the catalyst bed at a temperature of 450 °C for 22 h. This degree of conversion was constant even after 28 h of continuous flow-circulation, as experimental controls showed (Fig. 1). It should be mentioned that methane conversion into C_2 hydrocarbons was initiated at 330 °C. Table 1 summarises the composition of the methane conversion products. As can be seen, after methane flow-circulation for 1 h a conversion of about 4.5% was reached, yielding predominantly ethylene and ethane (92.9%). After prolonged reaction time an increase of C_2–C_4 olefins of around 70–75% was observed, 50–55% of which was ethylene. At this point, the level of hydrogen in the reaction volume was not more than 0.01% according to GC (LKhM-8MD and Biokhrom chromatographs) and MS (VIMS MS-7201) analyses.

Analysis by X-ray (DROM-3M, Cu-Kα) diffraction of the composition of the catalyst showed that, in addition to the reflections corresponding to the metal titanium phase [d = 2.24; 2.34; 2.55 A], titanium chips removed from the reactor under anaerobic conditions showed well-resolved intense reflections

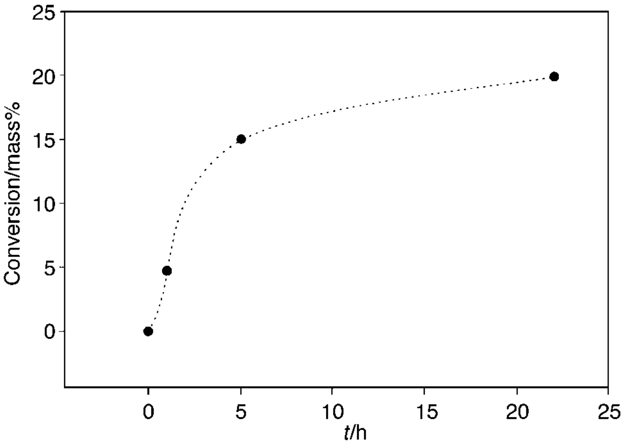

Fig. 1 Conversion of methane into products summarised in Table 1.

Table 1 Methane conversion and the composition of products from its transformation (T = 450 °C, P = 10 atm)

Composition (% mass)	Composition (mass%)			
	1 h	5 h	22 h	28 h
CH_4	95.3	85.3	79.8	80.1
C_2H_4	2.5	8.2	10.0	10.8
C_2H_6	1.9	3.0	4.8	4.4
C_3H_6	0.1	2.5	3.1	2.1
C_3H_8	0.2	0.4	0.4	0.3
C_4H_8	< 0.1	0.4	1.3	1.7
C_4H_{10}	< 0.1	0.2	0.6	0.6

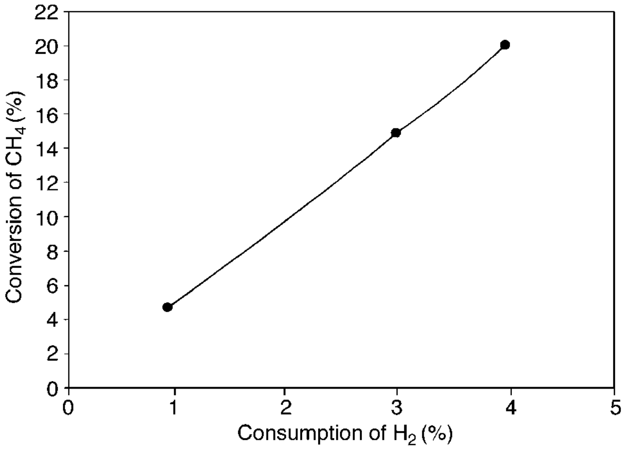

Fig. 2 Dependence of methane conversion on the quantity of hydrogen evolved and sorbed by the heterogeneous system.

due to a hydride phase (TiH_2) [d = 2.22; 2.31; 2.53 A]. At the same time, the reflections associated with the metal titanium phase shifted by only 0.45–0.47° (2θ) with respect to the starting system for the porous titanium. This evidence for the formation of a Ti–H interstitial solid solution during the decomposition of methane.

Fig. 2 shows that the increase in the methane conversion, in the range of operation, is proportional to the amount of hydrogen sorbed by the system, this being calculated on the basis of the stoichiometry of the reaction. This enables us to conclude that the removal of hydrogen from the reaction zone is, as expected, one of the main stages of the transformation of methane into higher products.

On the basis of the balance of the identified products, we may propose the pathways in eqns. (1)–(4) for the self-interaction reactions between the intermediates formed from methane activation.

$$2\,CH_4 \rightarrow 2\,[CH_2^*] - 4\,[H] \rightarrow C_2H_4 \qquad (1)$$

$$2\,CH_4 \rightarrow 2\,[CH_3^*] - 2\,[H] \rightarrow C_2H_6 \qquad (2)$$

$$3\,CH_4 \rightarrow 3\,[CH_2^*] - 6\,[H] \rightarrow C_3H_6 \qquad (3)$$

$$3\,CH_4 \rightarrow [CH_2^*] + 2\,[CH_3^*] - 4\,[H] \rightarrow C_3H_6 \qquad (4)$$

The C_4 fraction is probably a result of ethylene dimerization. We also propose that one of the limitations of this process is the coordination of CH_2^* intermediates to the surface metal centres. The interaction between closely coordinated [CH_2–M] species at the catalyst surface could be followed by their elimination leading to ethylene formation. In this way we can explain the high selectivity for C_2 alkene. In fact this tentative mechanism for the formation of olefins is in good accordance with the concepts of metal complex homogeneous catalysis.[6]

In any case our results indicate that C_2–C_3 species can be obtained by a single step, compared with direct or indirect processes which involve multi-steps such as the syngas and steam reactions. Of course, the problem of the hydrogen spillover to the titanium chips requires further study, which is now in progress.

Here we have reported a new finding which opens the way to selective low temperature methane conversion to important products by a new means using bifunctional hydrogen accumulating systems. At the same time the process offers the possibility of simultaneously obtaining high purity dihydrogen.

The authors acknowledge the Russian Science Foundation (Project 970332028a), NATO (Project ref. ENVIR.LG 971292) and DGICYT-Spain (Project PB96-1346) for supporting part of this work.

Notes and references

1 J. M. Fox, *Catal. Rev.-Sci. Eng.*, 1993, **35**, 169.
2 A. Ye. Shilov and G. B. Shulpin, in *Activation and Catalytic Reactions of Hydrocarbons*, ed. A. P. Purmal, Moscow, 1995, p. 399.
3 *Methane*, ed. F. A. Alekseev, Nedra, Moscow, 1978.
4 D. R. Stull, E. F. Westrum and G. C. Siuke, in *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
5 J. H. Ross, in *Metal Catalysed Methanation and Steam Reforming*, in *Catalysis*, ed. G. C. Bond and G. Webb, The Royal Society of Chemistry, London, 1985, vol. 7, p. 1.
6 M. L. H. Green, *Organometallic Compounds*, in *The Transition Elements*, Methuen, London, vol. 2, 1968.

Communication 9/01439J

Typeset and printed by Black Bear Press Limited, Cambridge, England