ELSEVIER

Catalysis Today 42 (1998) 333–336

CATALYSIS TODAY

Methane processing under microwave radiation: Recent findings and problems

Yuri Yu. Tanashev*, Viktor I. Fedoseev, Yuri I. Aristov, Vladimir V. Pushkarev, Lyudmila B. Avdeeva, Vladimir I. Zaikovskii, Valentin N. Parmon

Boreskov Institute of Catalysis, 630090 Novosibirsk, Russian Federation

Abstract

Microwave-driven transformations of methane and methane-containing mixtures in the presence of microwave-absorbing objects have been investigated. Application of pulse microwave (MW) power is shown to be a promising way for the production of hydrogen, syngas, acetylene and filament carbon. The influence of catalyst nature, MW-power and contact time on the reaction rate is analyzed. Two pathways for the studied reactions are found – a direct MW-heating of the whole catalyst (or its active centers) and a gas discharge near the rough catalyst surface. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane conversion; Microwave-driven catalysis

1. Introduction

The great resources of natural gas result in a large body of researches on methane processing into valuable chemical products. It is well known that selective transformation of methane into C_n-hydrocarbons ($n \geq 2$) meets a lot of problems because it requires high temperatures, a great deal of energy, the necessity of special catalysts, etc. A set of promising non-traditional methods for natural gas conversion is under extensive development, one of them is the use of MWs as a source for methane activation. The method advanced so far is the plasmochemical methane conversion with a MW generator used to keep a plasmatron operation. Direct use of MWs in catalysis was applied lately [1,2]. Since the energy of MW quanta is far insufficient for direct electronic excitation of reagents or breaking chemical bonds, MW heating is considered to be the most probable way for activating solid catalysts. MWs easily penetrate materials (except for metals) and can be absorbed by the whole volume of an irradiated object, causing its fast and homogeneous heating. Another approach to MW catalysis is based on the idea of selective heating of an active metal supported on a porous dielectric matrix. A ceramic catalyst support therewith does not absorb MWs and remains cold thus providing fast quenching of reaction products [1].

In this communication we present our experimental results on methane processing via continuous and pulse MW action on different catalysts and other solid additives. Some factors influencing the process (catalyst nature, level of the MW-power, gas residence time) have been analyzed.

---

*Corresponding author. Fax: +7 383 2 34 46 87; e-mail: tanashev@catalysis.nsk.su

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0920-5861(98)00110-2

2. Experimental

A magnetron M-117 (former USSR) of 2.45 GHz frequency and of generated power up to 5 kW operating under both continuous and pulse modes was used as a MW source. Pulse duration t_p and frequency ν were ranged within 1–100 ms and 0.5–125 Hz. A tubular quartz reactor with a fixed catalyst bed was placed directly into the rectangular waveguide at an angle of 28° to its broad wall.

Various commercial (GIAP-16, RK-3, porous Ni) and lab-synthesized (alloy Al–Ni–Ti, ThO_2/Al_2O_3, Fe/Al_2O_3, Ni/Al_2O_3-1, Ni/Al_2O_3-2, porous Ni+Fe, Fe+Al) catalysts for the methane activation as well as steel and copper wires of 0.25–1.0 mm thickness were tested under MWs. The synthesized alumina-based catalysts were prepared by impregnating α- and γ-Al_2O_3 with a large excess of proper salt solution and a consequent drying. Ni-containing catalysts were reduced in hydrogen at 400°C before reaction performance.

Reagent flow was varied from 0.5 to 5 cm^3/s at total pressure 100–120 kPa. The reaction products were analyzed by using a gas chromatograph LXM-8MD. The sensitivity to gaseous reaction products was the following (in vol%): $H_2 - 10^{-3}$, $C_2H_2 - 5\cdot10^{-2}$, $C_2H_4 - 10^{-1}$, $C_2H_6 - 5\cdot10^{-1}$, $C_3H_8 - 10^{-1}$. Condensed products were analyzed by a chromato-mass-spectrometer LKB 2091 (Sweden). Finally we calculated the rate and the selectivity of the processes under study:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad (1)$$

$$CH_4 \rightarrow C + 2H_2 \quad (2)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad (3)$$

Blank experiments with the empty reactor and common heating by an electric oven are done for comparison with the MW-catalytic action [3]. More experimental details may be found elsewhere [4].

3. Results and discussion

Our preliminary experiments on the catalytic methane processing under MW radiation have been aimed to establish guidelines for experimental conditions influencing the process, namely, catalyst nature, level of MW-power and pulse envelops, reagent residence time, etc.

A choice of the catalyst for a MW-driven process appears to be of great importance as it must meet some specific requirements in addition to the common demands of high activity, selectivity, stability, etc. Evidently such a catalyst has to be a good receptor of MW energy and not to change its structure and properties under intense MW-radiation. Although MW absorption by small dielectric and metal particles has received strong attention [5,6], so far a synthesis of catalysts for the MW-chemistry is driven by intuition rather than by exact knowledge.

Unfortunately, we have found that many commercial supported catalysts of the methane activation demonstrate rather poor MW-absorbency, and thus can hardly be used in practice. A possible way to improve interaction between MWs and active centers of irradiated surface is the preparation of special catalysts with increased size and amount of MW-absorbing particles. We have synthesized the catalysts m-Ni/Al_2O_3 (m>40 wt%) with separate Ni-particles of about 20 nm size uniformly distributed over the sample. The catalysts, tested in reaction (1), are shown to allow a combination of both the demands mentioned above. They provide an appreciable methane conversion $x>0.5$ under both continuous and pulse modes. Even more active is the multi-phase porous Al–Ni–Ti alloy which also possesses a very high MW-absorbency. As a measure of MW activity the value of specific power loading $w=W_{chem}/V$ (where W_{chem} is the enthalpy change during reaction per unit time, V is the catalyst volume) may be used. In the case of oven heating the sufficient thermal resistance between the wall and the catalyst bed together with the low thermal conductivity of the catalyst lead to a limitation of the heat flux and, therefore, of the specific power loading by the values of about 5–10 W/cm^3 [7]. On the contrary, the direct MW heating leads to removing the limitation; for reaction (1) the w value is measured to achieve 40 W/cm^3 for Al–Ni–Ti at $x\approx0.5$.

For these well-absorbing catalysts the average MW power may strongly influence the rate of methane activation (Fig. 1). Pulse MW power and a structure of the pulse envelops are also of importance and give an efficient tool for management and control of the MW-driven catalysis.

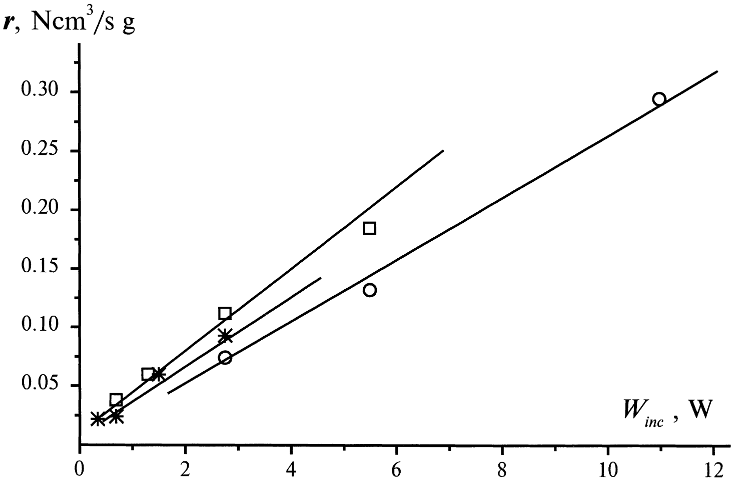

Fig. 1. The rate r of methane conversion as a function of the average incident MW power W_{inc}. Conditions: reaction (1) in the presence of the grid made from the stainless steel wire, the wire diameter=0.25 mm, mass of the grid=0.95 g, the reactor volume=0.8 cm^3, CO_2:CH_4=4, the pulse MW mode (t_p=1 ms), the methane conversion x=0.25 (*), 0.5 (□), and 0.75 (○).

As in the common catalysis, an increase in the ''gas-catalyst'' residence time τ generally gives a rise of the MW-induced methane conversion x up to its equilibrium value. However, in several cases a quite unusual opposite dependence $x(\tau)$ is observed that is likely to indicate that the powerful MW-radiation generates an extra-equilibrium product concentration which is then going down to its thermodynamic value while the residence time increases (see also [4]).

MW power can be also used for methane processing into pure hydrogen and filament carbon (Fig. 2) which is of high practical interest because of its prominent adsorption properties. This reaction takes place on lab-synthesized Ni- and Fe-containing catalysts. Under

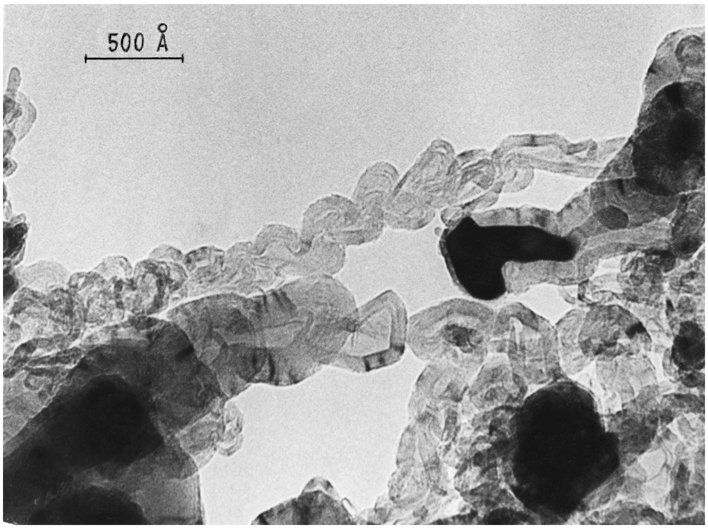

Fig. 2. TEM micrograph of filament carbon as a product of MW reaction (2) on lab-synthesized porous Fe+Al catalyst. Conditions: ''gas-catalyst'' residence time=0.1 s, the pulse MW mode (t_p=2 ms, ν=8 Hz).

pulse mode the value V_c/V (V_c – volume of deposited carbon) may quickly achieve 1, much faster than under common heating.

Another distinctive feature of the MW-catalysis is a possibility for a new channel of methane processing to appear due to electric gas discharges in the vicinity of the rough catalyst surface. The discharge reaction mode can be realized at low average (but high pulse) MW power, when $t_p<8$ ms and $\nu<16$ Hz, whereas the conventional MW-heating of the catalysts predominantly takes place at high average power. The experiments show a high rate (>10 N cm^3/s.g) of the methane conversion to hydrogen and acetylene under gas discharge in the presence of stainless steel or copper grid as ''a catalyst''. The selectivity of the process is found to be higher than 50%. The rate of acetylene formation increases if argon, which is a good ''discharge conductor'', is added to methane at the reactor inlet in the amount of up to 50 vol%. If $t_p>8$ ms and $\nu>16$ Hz, the discharge flashes disappear and tangible heating of the irradiated catalysts occurs. The yield of acetylene is severely decreased, whereas the yield of hydrogen remains almost unchanged. Simultaneously, the formation of small amount of ethylene, ethane and condensed products is observed. The product composition is close to that for common high temperature pyrolysis of methane [3].

In closing it may be said that despite the problems we met (formation of coke as by-product in reactions (1) and (3), respectively low efficiency of MW energy conversion) the application of MW power may open up fresh opportunities for methane processing. Based on the results obtained one can expect that even in the near future the development of MW-absorbing metal-based catalysts and MW technique will result in creation of a new generation of devices for utilization of natural gas.

Acknowledgements

The work is partially supported by grants of the Russian Department of Education on the Programs ''Basic research in the field of Chemical Engineering'' and ''Non-traditional methods in Chemical Engineering''.

References

[1] J. Wan, M. Tse, H. Husby, M. Depew, J. Microwave Power and Electromagnetic Energy 25 (1990) 32.

[2] J.-M. Thiebaut, G. Roussy, M. Medjram, F. Garin, L. Seyfried, G. Maire, Catal. Lett. 21 (1993) 133.

[3] V.I. Fedoseev, Yu.I. Aristov, V.N. Parmon, Abstracts 2-nd Workshop Meeting C_1–C_3 Hydrocarbon Conversion, Krasnoyarsk, 1994, p. 64.

[4] Yu.I. Aristov, V.I. Fedoseev, Yu.Yu. Tanashev, V.V. Pushkarev, V.N. Parmon, in: Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, 23–28 June 1996, vol. 1, p. 931.

[5] P. Marquardt, Phys. Lett. A 123 (1987) 365.

[6] G.D. Mahan, Phys. Rev. B 38 (1988) 9500.

[7] Yu.I. Aristov, V.N. Parmon, in: Photocatalytic Solar Energy Conversion (in Russian), Nauka, Novosibirsk, 1991, p. 257.