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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Production of a Highly Dispersed Carbon Material and Hydrogen from Natural Gas in a Microwave Reactor with Metallic Catalysts

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Abstract—Effect of a microwave field on metallic catalysts was studied in the reaction of decomposition of methane into hydrogen and highly dispersed carbon. The dependence of the conversion of methane, yield of carbon, and its composition on the chemical nature of a catalysts and reaction conditions was examined.

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One of the most important problems of rational use of hydrocarbon raw materials consists in utilization of low-pressure natural gas and petroleum gases. It is commonly believed that the most promising, in addition to burning in flares, are the gas-to-liquid conversion (GTL) and(or) burning to produce electric power [1].

Generation of electric power at production sites seems to be rational, but requires capital investment with nearly zero payoff because the amount of generated power markedly exceeds the needs of oil fields and a problem arises of utilizing the excess electric power. In this case, it is promising to construct, together with power plants, power-consuming installations for processing of a gas into easily transportable products. At present, new processes are required for conversion of methane into valuable products in order to use in due way resources of natural and petroleum gases. This is particularly topical because of the development of the hydrogen power engineering, in which natural gases are regarded as the main raw materials for production of hydrogen.

The thermal conversion of methane may occur by the following endothermic (energy-consuming) reactions [2]:

$$CH_4(g) = C(s) + 2H_2(g),\ \Delta H_{1300\,K} = 92.11\text{ kJ}; \quad (1)$$

$$2CH_4(g) = C_2H_4(g) + H_2(g),\ \Delta H_{1300\,K} = 108.86\text{ kJ}; \quad (2)$$

$$2CH_4(g) = C_2H_2(g) + 2H_2(g),\ \Delta H_{1300\,K} = 406.12\text{ kJ}. \quad (3)$$

In addition to the target reaction (1) of hydrogen formation, also possible are reactions (2) and (3). In this case, it is rather promising to employ combined processes of physical treatment and catalysis, i.e., catalysis combined with exposure of the catalyst and methane to a microwave field [3].

EXPERIMENTAL

Experiments were performed in the installation shown schematically in Fig. 1. Natural gas was converted in a flow-through quartz reactor of a waveguide type with an inner diameter of 18.5 mm in the presence of a microwave discharge at a frequency of 2450 MHz. The discharge was maintained and the catalyst was heated (300–650°C) with a microwave generator operating in the continuous mode with an output power finely adjusted in the range 700–1500 W. The temperature was measured with a Kel’vin KB-Dipol’ noncontact IR thermometer with a measurement range 200–2000°C. As catalysts served bulky granulated metals (Ni, Fe, Mo) and intermetallic compounds

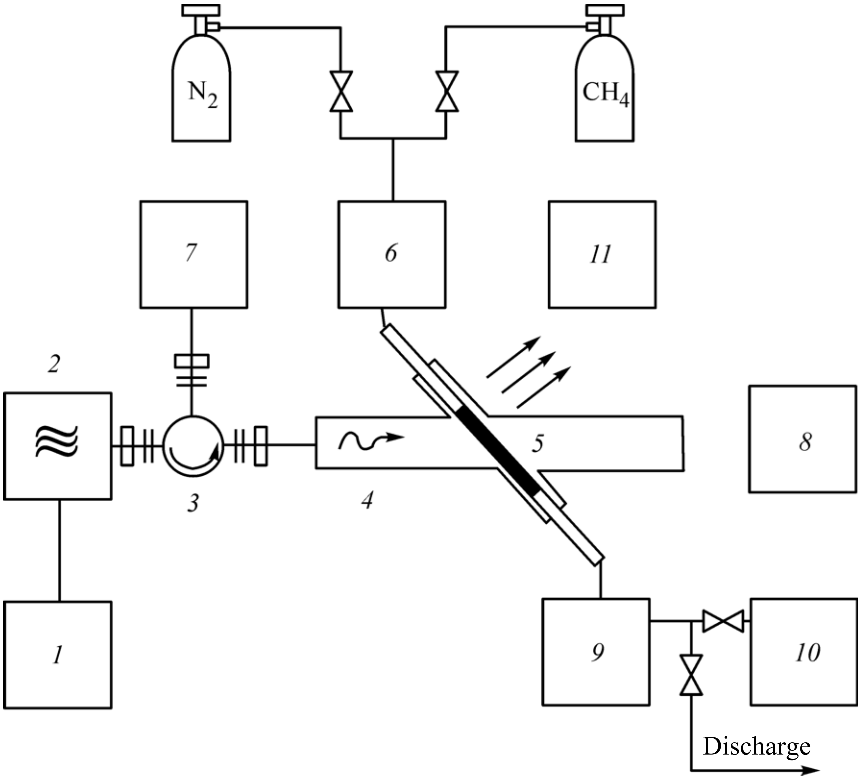

Fig. 1. Schematic of laboratory installation. (*1*) Power source of the microwave generator, (*2*) microwave generator, (*3*) circulator, (*4*) waveguide, (*5*) reactor, (*6*) gas flow control valve, (*7*) meter of reflected microwave power, (*8*) meter of transmitted microwave power, (*9*) carbon collector, (*10*) gas-mixture-sampling unit, and (*11*) pyrometer.

(TiNI and AlNi) with a grain size of 0.1–2 mm. As raw materials was used natural gas containing 94 vol % CH_4 and C_2-hydrocarbons the rest.

A chromatographic analysis of gas mixtures was made on a Khromatek-Kristall 5000.1 chromatograph with DTP and PID detectors and the following columns: HP-PLOT capillary column (50 m) with supported Al_2O_3/KCl, packed column (2 m) with Carbosieve S-II sorbent (60–80 mesh), and packed column (3 m) with NaX sorbent (60–80 mesh). The thermostat temperature was 80°C, as carrier gases served helium and argon. The concentrations of the gas mixture components were calculated by the absolute-calibration method with Khromatek Analitik 2.5 software.

The specific surface area of the carbon product was measured by the multiple-point BET method with a Sorbi 4.1 instrument. Surface micrographs of carbon samples were obtained with a Philips SEW 515 scanning electron microscope. X-ray diffraction analyses of the samples were made on a Shimadzu XRD 6000 X-ray diffractometer.

The catalysts used in the study belong to “bulk metals.” When a catalyst is exposed to a microwave field, two processes occur simultaneously. First, catalyst grains are heated under the action of the microwave energy because of the dissipative loss. In the experiments, the samples are heated to temperatures of 300–650°C. These values fall within the temperature range characteristic of catalytic methods for synthesis of nanosize carbon (nanofibers, nanotubes) from methane [4, 5]. Second, “partial” electric discharges (microdischarges) between grains are caused by induced electromagnetic fields when a catalyst is exposed to a microwave field. This promotes decomposition of methane to unsaturated hydrocarbons by reactions (2) and (3). For example, a similar effect of the microwave field on methane to give acetylene was observed in [3], with metallic catalysts or grids used. It is also probable that nanotube precursors are formed on the surface of metallic catalysts by reaction (1). All the reactions mentioned above are endothermic. That is why, when nitrogen, in whose flow the catalyst is heated, is replaced in gas

Table 1. Parameters of conversion of natural gas, composition and properties of the carbon product

Catalyst composition	Methane conversion, %	Yield of carbon per passed methane, %	Content, %		Specific surface area, $m^2 g^{-1}$	H_2 concentration, vol %	Content of C_2-hydrocarbons, vol %
			amorphous carbon	nanotubes			
TiNi	42.4	11.2	45.00	46.1	20.9	52.3	8.8
AlNi	15.8	23.5	55.00	33.1	18.7	28.3	2.2
Ni	79.5	62.9	21.2	56.5	42.9	84.9	4.0
Fe	54.5	46.7	4.04	78.2	69.7	69.4	2.2
Mo	77.6	35.9	64.9	24.9	19.5	84.6	3.1

Table 2. Types and SCR-based sizes of nanotubes being formed

Catalyst composition	Nanotubes					
	multi-walled		single-walled		onion-like	
	amount, %	SCR-based size, nm	amount, %	SCR-based size, nm	amount, %	SCR-based size, nm
TiNi	100	9.1	–	–	–	–
AlNi	100	10.6	–	–	–	–
Ni	19.4	14.9	45.0	7.8	35.6	7.1
Fe	28.2	12.4	38.8	7.3	33.0	3.7
Mo	47.0	26.3	32.9	37.2	20.1	37.2

flows with methane, the temperature of the catalyst bed decreases by 20–80°C relative to the initial value, with this decrease dependent on the amount of methane fed into the reactor (residence time).

Reactions (1)–(3) result in that hydrogen and unsaturated hydrocarbons accumulate in reaction gases, as also do particles (precursors) of carbon. Accordingly, ingress of products formed in decomposition of methane into a gradient microwave field favors formation of a plasma jet fed by the microwave energy at the exit from the catalyst bed. Under gas discharge conditions, there occur fast chemical transformations of natural gas (methane) into carbon, hydrogen, and unsaturated hydrocarbons [6]. About 80% of the microwave power is consumed for maintaining the plasma jet, and 10–15%, for maintaining the temperature in the catalysts bed. Therefore, it can be assumed that the main conversion of methane occurs in the plasma being formed.

The conversion of methane and the amount and size of nanotubes in the carbon product are determined by the chemical nature of a catalyst (Tables 1, 2). The varied chemical nature of metallic catalysts can affect their electrical properties, and, accordingly, the effect of a microwave field on the bulk of the catalyst bed and the nature of “microdischarges” may change. The chemical composition of catalysts can affect the structure of precursors of dispersed carbon, formed in the process. It was shown in [4, 5] that the chemical composition of methane decomposition catalysts affects both the conversion of methane and the structure of a carbon product being formed. According to the data in Table 1, the conversion of methane is low with AlNi and TiNi intermetallic compounds as catalysts, with only multi-walled nanotubes found in the carbon product (Table 2).

When Ni and Fe catalysts used for decomposition of methane and formation of carbon [4, 5], the conversion of methane increases and the content of nanotubes becomes larger than that in amorphous carbon (Table 1), with three types of nanotubes observed (predominantly single-walled and onion-like) (Table 2). According to [7], metallic molybdenum supported by a high-silica zeolite is an effective catalyst for activation of methane to give ethane and ethylene, but carbon formed on the surface of

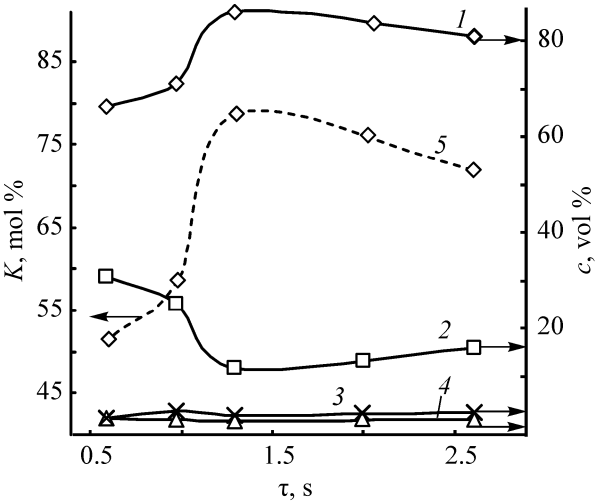

Fig. 2. Effect of the contact duration τ on the concentrations *c* of (*1*) hydrogen, (*2*) methane, (*3*) acetylene, and (*4*) ethylene and (*5*) on the conversion *K* of methane.

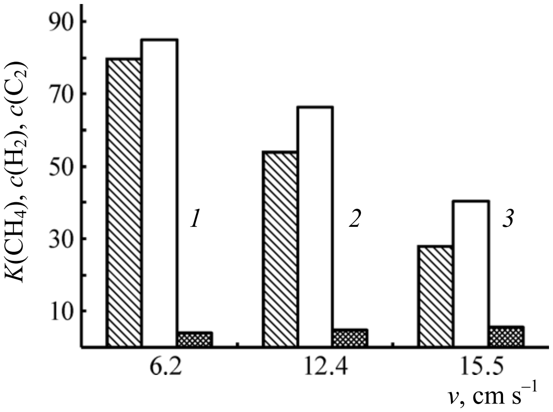

Fig. 3. Dependence of (*1*) methane conversion $K(CH_4)$ and concentrations of (*2*) hydrogen [$c(H_2)$] and (*3*) C_2 hydrocarbons (ethylene, ethane) [$c(C_2)$] on the linear flow velocity ν of methane.

molybdenum particles has a graphite-like structure. According to the data in Table 1, a high conversion of methane is observed with Mo, and the yield of the carbon product and nanotubes is low, compared with other samples of metallic catalysts.

Combination of catalytic and plasmochemical processes leads to complex dependences in the endothermic reactions of methane decomposition. Making shorter the time of contact with the catalyst at a constant linear flow velocity of methane diminishes the conversion of methane and the concentration of hydrogen, the concentration of C_2-hydrocarbons being constant (Fig. 2). Raising the linear flow velocity of methane markedly diminishes the conversion of methane and the yield of hydrogen and raises the concentration of C_2-hydrocarbons in reaction gases (Fig. 3).

Table 1 lists concentrations of hydrogen and byproducts (ethylene, acetylene) obtained in a single pass of the reaction mixture. The highest conversion of methane and concentration of hydrogen in reaction gases are observed on nickel and molybdenum catalysts, and the highest yield of carbon nanotubes is characteristic of Ni and Fe.

The carbon product is predominantly composed of amorphous carbon and carbon nanotubes, with a minor amount of graphite, orta carbon, and fullerenes. Orta carbon is formed only on Ni-containing catalysts (Ni, AlNi, and TiNi). The chemical composition of the catalyst (Table 2) strongly affects the type of nanotubes being formed, their relative amounts, and sizes determined from the coherent scattering region (CSR), which vary with the range 9.1–26.3, 7.3–37.2, and 3.7–37.2 nm for multi-walled, single-walled, and onion-like nanotubes, respectively. The specific surface area of the carbon product varies from 18.7 to 69.7 m^2, depending on the catalyst used.

With the supply rate of raw materials and catalyst composition varied, it is possible to obtain carbon materials with different relative amounts of nanotubes and amorphous dispersed carbon. The most frequently encountered problem of the catalytic synthesis of carbon is occlusion of catalyst particles by the carbon product. Occluded metal particles are not dissolved in acids and contaminate nanotubes and nanofibers [8]. In a microwave reactor, precursors of nanotubes and nanofibers, formed on the catalyst surface, are carried by the hydrogen plasma into the discharge zone and contain no metal, which makes unnecessary the stage of washing of the carbon product to remove the metal or metal oxides.

Figure 4 shows micrographs of carbon, from which it is seen that the product obtained can be conditionally divided into two kinds: the first structure is formed by associates with “cotton wool” structure and sizes of 10–20 μm (Figs. 4a–4c), constituted by finer structures 200–250 nm in size (Fig. 4); the smallest among the observed particles, 30–40 nm in size, form disordered associates (Fig. 4c). Probably, this is amorphous carbon, whose content in the final product may reach a value of 64.8% (Table 1) in the case of a Mo-system. The second structure of carbon being formed are nano-

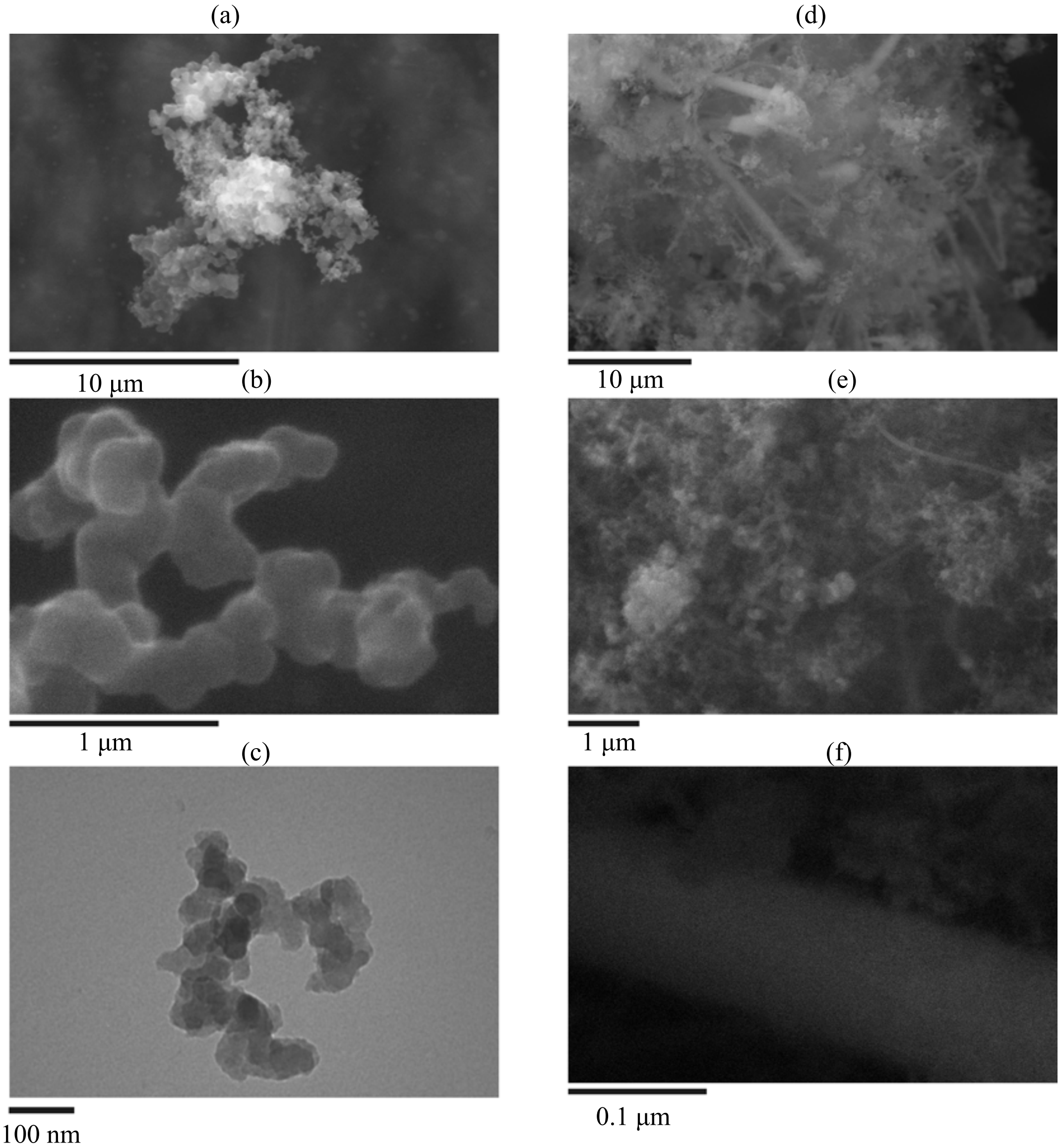

Fig. 4. Micrographs of samples of the carbon product obtained. Associates of "cotton wool" texture with sizes (μm): (a) 10–20, (b) 200–250, (c) 30–40; (d) fibrous carbon; (e) fibrous carbon distributed over the surface of "cotton wool" associates; and (f) carbon fiber with a diameter of 100 nm.

fibers that may be chaotically interweaved (Fig. 4d) or redistributed over the surface of "cotton-wool" associates (Fig. 4e). The diameter of carbon fibers is, on average, 100 nm (Fig. 4f). Unfortunately, the instrument gives no way of studying finer forms of the carbon, which are apparently present in the carbon product.

In recent years, studies have been performed in order to develop and commercialize power installations based on fuel cells with a proton-exchange membrane (PEMFCs). Hydrogen serves as a fuel for PEMFCs, with atmospheric oxygen serving as the oxidizing agent. Wide introduction of PEMFCs encounters a number of difficulties, one of which is the necessity for effective reduction of the concentration of CO ("poison" for a fuel cell) to 10–100 ppm in the hydrogen-containing gas. Because the presently employed techniques for production of hydrogen from natural gases are based on selective oxidation of methane to synthesis gas, conversion with steam, or a combination of these, the resulting hydrogen is always contaminated with CO, which requires an additional stage of catalytic purification [9]. In the case of carbon synthesis in a microwave reactor, the resulting hydrogen contains no CO and residual unsaturated C_2-hydrocarbons are rather easily separated from hydrogen, which will make it possible to obtain high-purity hydrogen.

CONCLUSIONS

(1) The process described is based on combined effects of the microwave radiation. These are heating of the catalyst and initiation of microdischarges in the catalyst bed, which excite gas molecules to give methane decomposition products. The microwave radiation also maintains the plasma jet, in which natural gas is fully decomposed and conversion products are removed from the reactor space.

(2) The capacity in terms of highly dispersed carbon at an average methane conversion of 70% is 0.3–0.5 g h^{-1} from a cubic centimeter of the reactor.

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