

Promoted Iron Catalysts of Low-Temperature Methane Decomposition

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Abstract

Iron-containing catalysts promoted by nickel or cobalt were tested in methane decomposition reaction at low temperature (600–650 °C) and pressure 1 bar in order to study their catalytic properties and to produce catalytic filamentous carbon (CFC). Catalyst preparation method and composition of the catalysts were found to influence their properties. It was found, that introduction of cobalt or nickel in small amount (3–10 % mass) results in the magnification of carbon yields 2–3 times in comparison with Fe-Al₂O₃. Investigations of Fe-Co-Al₂O₃ and Fe-Ni-Al₂O₃ catalysts genesis were performed by Mössbauer spectroscopy, XRD, TEM. It is established that Co or Ni additives render activating influence on Fe catalysts which become apparent in decrease of the methane decomposition temperature and the formation of multiwall carbon nanotubes (MWNTs).

INTRODUCTION

The increase of CO₂ concentration (a major greenhouse effect gas) in the atmosphere due to the use of fossil fuels such as petroleum, natural gas and coal leads to change in the planet's climate, so we have to develop a new energy production systems which decrease the CO₂ emission. From this point of view H₂ is a clean fuel that emits no CO₂ when it is burned or used in H₂-O₂ fuel cells. At present, many catalysts of methane transformation have been widely investigated because of their importance in the utilization of natural gas and production of H₂ [1]. Numerous studies of Ni, Fe, Co catalysts in steam reforming, hydrocarbon decomposition have shown that formation of filamentous carbon with graphitic structure – catalytic filamentous carbon (CFC) occurred [2–13]. Realistic way to produce hydrogen considers decomposition of methane, the main component of natural gas, into carbon and hydrogen without CO₂ emission. The hydrogen is used as a clean energy (or a fuel for fuel-

cells) and the carbon should be used for synthesis of useful chemicals through synthesis-gas production by water gas reaction. The carbon can be also used as the functional material such as composites, electrodes, catalyst supports, adsorbents *etc.*

It was shown, that Ni and Co catalysts exhibit essential efficiency in CFC accumulation and methane conversion is close to equilibrium at temperatures 500–550 °C. We found that a large amounts of filamentous carbon can be produced using coprecipitated catalysts: the 90 % mass Ni-Al₂O₃ yields 110 g/g_{Ni}, 75 % mass Co-Al₂O₃ – 60 g/g_{Co}. The CFC is usually formed as the granules of chaotically interlaced filaments or fibers. One carbon filament grows from one catalytic particle, the latter being located on its top. Carbon filament consists from graphitic planes which are coaxially arranged as cones. Average diameter of the carbon filament for Ni-based CFC is 50 nm, for Co-based – 20 nm. The nature of catalyst influences the microstructure of filament, that becomes apparent in the angle between graph-

itic planes and the filament axis, which varies from 45° for Ni catalyst [10] to 15° for Co catalyst [11]. The copper addition into Ni catalyst changes the crystallographic orientation of the catalyst particles and as a consequence changes microstructural and textural properties of formed CFC. As a result, the thermal stability and carbon capacity (which can reach 700 g/g_{Ni}) of Ni-Cu increase [12]. Earlier the methane decomposition over iron-contained catalysts was investigated at temperatures above 800 °C with the purpose of deriving hydrogen [14] or carbon fibers [15]. However the developed iron catalysts were soon deactivated. Recently it was shown that CFCs were formed at methane decomposition over 85 % mass Fe-SiO₂ catalyst at temperature not lower than 680 °C [16]. It has been established that Co additives render activating influence on Fe catalysts which become apparent in decrease of the methane decomposition temperature and the formation of multiwall carbon nanotubes (MWNTs) [17, 18].

The main purpose of the given work is development of the long-living promoted by Ni and Co iron-containing catalysts of methane decomposition and carbon accumulation at low temperatures. In this paper we investigate the activity of coprecipitated Fe-Al₂O₃, Fe-Ni-Al₂O₃ and Fe-Co-Al₂O₃ catalysts, as well as the structure and texture of the formed CFC.

EXPERIMENTAL

Fe-Al₂O₃, Fe-Ni-Al₂O₃ and Fe-Co-Al₂O₃ catalysts were prepared by a coprecipitation method from a solution of metal nitrates using different precipitants. The coprecipitated samples were carefully washed with distilled water, dried at 110 °C, and calcined in a flow of air at 450 °C for 3 h. The catalysts were reduced in a flow of pure hydrogen at 580 °C for 5 h, then the samples were in situ passivated in ethanol and dried at room temperature.

Catalytic activity of the reduced samples was measured in a vibrating flow quartz reactor 30 cm³ in volume. Methane was supplied at a rate of 45 l/(g_{cat} h). Concentration of methane was measured by gas chromatography, and methane conversion was calculated. To deter-

mine the amount of carbon deposited, sample was weighted after the reaction, which was performed until complete catalyst deactivation.

The samples of catalysts and CFC were investigated by TEM, Mössbauer spectroscopy, XRD and adsorption methods. The XRD studies were performed in a Siemens URD-63 diffractometer using CuK_α radiation and a graphite crystal monochromator. Crystallite sizes were calculated from the line width of diffraction peaks (110) for α-Fe, (440) for Fe-Co-Al spinel and (002) for graphite following the Scherrer equation. Mössbauer spectra were obtained by using constant-acceleration NZ-640 (Hungary) spectrometer with a ⁵⁷Co in Rh source. Isomer shifts were reported relative to α-Fe at room temperature. TEM and HRTEM pictures were obtained with JEM-100CX and JEM-2010 microscopes respectively. The adsorption measurements were carried out using an ASAP-2400 apparatus to provide adsorption of N₂ at 77 K.

RESULTS AND DISCUSSION

In order to compare the carbon formation efficiency of prepared catalysts, we use the following parameters of the methane decomposition reaction: methane conversion, carbon accumulation until complete deactivation of the catalysts (the so-called carbon capacity *G*, calculated as gram of carbon per gram of a catalyst) and lifetime of the catalysts.

Effect of catalyst preparation method

Earlier we have shown, that for high-loading catalysts the method of coprecipitation from aqueous solution of the salts is more favorable. Moreover, studying the Ni-Al₂O₃ and Co-Al₂O₃ systems we have found, that the best catalytic performance was observed with the catalysts prepared using sodium hydroxide as a precipitant [10, 11]. In order to study an effect of the preparation method for Fe catalysts we vary a precipitant (NH₄OH, NH₄HCO₃, NaOH, Na₂CO₃) which, in principle, can lead to the different Fe precursors. Data are summarized in Table 1.

In contrast to Ni and Co catalysts, from Table 1 one can see that the greatest carbon ca-

TABLE 1

Catalytic properties of Fe-based catalysts for methane decomposition, demonstrating the influence of preparation methods ($T = 625$ °C, methane space velocity $45 \text{ l}/(\text{g}_{\text{cat}} \text{ h})$, $P_{\text{CH}_4} = 1$ bar, X_{CH_4} - methane conversion during 1 h)

Catalysts	Precipitant	X_{CH_4} , %	Lifetime, h	G , g/g _{cat}	Co or Ni, % mass (chemical analysis)
50 Fe-Al ₂ O ₃	NH ₄ OH	4	23	26.5	-
50 Fe-Al ₂ O ₃	NaOH	6	6	3.3	-
50 Fe-Al ₂ O ₃	Na ₂ CO ₃	4	6	2.3	-
90 Fe-Al ₂ O ₃	NH ₄ OH	5.2	7	5.5	-
85Fe-5Co-Al ₂ O ₃	NH ₄ OH	8	16.5	16.0	4.86
85Fe-5Co-Al ₂ O ₃	NH ₄ HCO ₃	7.7	16	16.0	4.89
85Fe-5Ni-Al ₂ O ₃	NH ₄ OH	10	16.5	13.5	-
85Fe-5Ni-Al ₂ O ₃	NH ₄ HCO ₃	6	16	12.9	3.66
85Fe-10Ni-Al ₂ O ₃	NH ₄ OH	10.3	15	17.6	3.03
85Fe-10Ni-Al ₂ O ₃	NH ₄ HCO ₃	7	16	14.9	6.63
85Fe-10Ni-Al ₂ O ₃	NaOH	10	11	11.9	8.22
85Fe-10Ni-Al ₂ O ₃	Na ₂ CO ₃	8	9	7.2	5.82

capacity of Fe-Al₂O₃ and Fe-Co-Al₂O₃ catalysts is observed for samples prepared by coprecipitation using aqueous solution of ammonia as a precipitant. In case of the Fe-Ni-Al₂O₃ catalysts ammoniac complexes of nickel are formed at coprecipitation by NH₄OH that results in incomplete precipitation of the components. We concluded that the best method of Fe-Ni-Al₂O₃ catalysts preparation is coprecipitation by NH₄HCO₃ solution and our studies were realized with catalysts prepared by the appropriate method.

Effect of the catalyst composition and temperature

Since the maximum carbon capacity during methane decomposition was observed for catalysts with the high metal loading (90 % mass Ni and 60–75 % mass Co), the iron content in coprecipitated Fe-Al₂O₃ catalysts has been varied from 20 to 90 % mass. The obtained values of carbon capacity are plotted in Fig. 1, *a* as a function of nominal bulk Fe concentration. Data show that carbon capacity reaches maximum (20–28 g/g_{cat}) on the catalysts with 50–80 % mass Fe. It is known, that Co or Ni additives (5–10 % mass) render activating influence on iron catalysts [19], therefore we have investi-

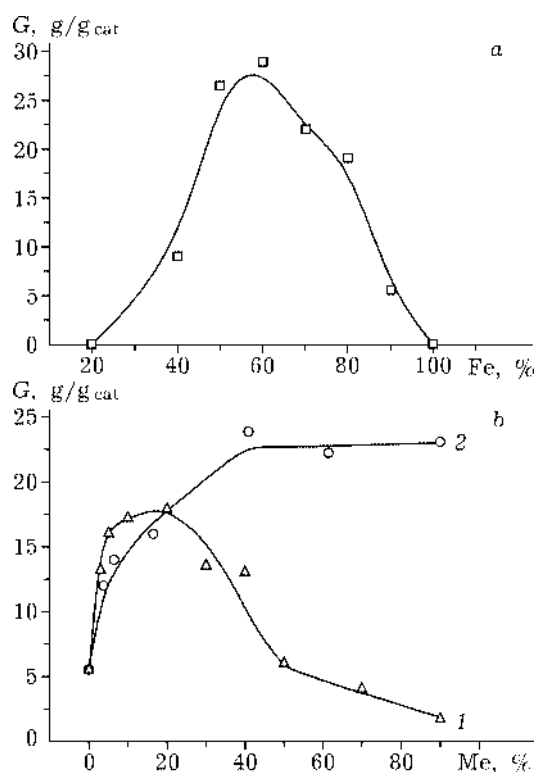


Fig. 1. The relationship between carbon capacity and metal loading in the coprecipitated Fe-Al₂O₃ catalysts, prepared using NH₄OH as precipitant (*a*) and second metal content in the Fe-Me-10 % mass Al₂O₃ (*b*): *a* - methane decomposition reaction at 625 °C, $P_{\text{CH}_4} = 1$ bar, methane space velocity = $45 \text{ l}/(\text{g}_{\text{cat}} \text{ h})$; *b* - Me = Co (1) or Ni (2).

TABLE 2

Catalytic properties of Fe-containing catalysts in the methane decomposition ($T = 625\text{ }^{\circ}\text{C}$, methane space velocity 45 l/(g_{cat} h), $P_{\text{CH}_4} = 1\text{ bar}$)

Catalysts	Fe : Me : Al ₂ O ₃ , % mass	Co or Ni, % mass (chemical analysis)	Lifetime, h	X _{CH₄} , %	G, g/g _{cat}
90Fe-Al ₂ O ₃	90 : - : 10	-	7	5.2	5.5
85Fe-5Co-Al ₂ O ₃	85 : 5 : 10	4.86	16.5	7.9	16
60Fe-30Co-Al ₂ O ₃	60 : 30 : 10	-	15	7.3	12.4
50Fe-Al ₂ O ₃	50 : - : 50	-	23	4	26.5
50Fe-6Co-Al ₂ O ₃	50 : 6 : 44	4.0	40	8	52.4
85Fe-5Ni-Al ₂ O ₃	85 : 5 : 10	3.66	16	6	12.9
80Fe-10Ni-Al ₂ O ₃	80 : 10 : 10	6.5	16	7	14.9
20Fe-70Ni-Al ₂ O ₃	20 : 70 : 10	61.4	4	33.9	22.3
90Ni-Al ₂ O ₃	0 : 90 : 10	-	4	34.8	23.1
85Co-Al ₂ O ₃	0 : 85 : 15	-	2	2	1.7

gated the influence of Co and Ni on Fe-Al₂O₃ catalysts of methane decomposition at 625 °C. Table 2 and Fig. 1, b show that introduction of Co or Ni in small amounts (3–10 % mass) results in the magnification of carbon yields 2–3 times. So, carbon capacity on the catalyst 50Fe-6Co-Al₂O₃ achieves 52.4 g/g_{cat}. An increase of nickel amount up to 45 % mass and above in the series of catalysts leads to the formation of catalysts with properties close to the properties of 90 % mass Ni-Al₂O₃. Apparently, the presence of Co or Ni increases the number of the carbon growth centers of the Fe-Al₂O₃ catalyst. The studies of temperature dependence of methane decomposition over 85Fe-5Co-Al₂O₃ catalyst have shown, that carbon capacity reaches its maximum at 625–650 °C (Table 3). The methane conversion at 650 °C reaches ≈ 13 %. Fig. 2 shows methane conversion *versus* reaction time for the Fe-containing catalysts at 625 °C.

TABLE 3

Temperature dependence of catalytic properties of 85Fe-5Co-Al₂O₃ catalyst (methane space velocity 45 l/(g_{cat} h), $P_{\text{CH}_4} = 1\text{ bar}$)

T, °C	X _{CH₄} , %	Lifetime, h	G, g/g _{cat}
550	3.0	13	5.1
600	5.1	8.5	6.7
625	8.0	16.5	16
650	12.9	13	15
675	10.9	8	13.2

Structure of catalysts

We performed XRD, Mössbauer spectroscopy and TEM studies of the calcined and fresh reduced Fe-Al₂O₃ and Fe-Co-Al₂O₃ catalysts, as well as of samples after their exposition to reaction mixture.

According to the XRD data calcined samples of Fe-Al₂O₃ and Fe-Co-Al₂O₃ are X-ray amorphous that testifies to formation of highly dispersed phase. The Mössbauer spectrum of the calcined 85Fe-5Co-Al₂O₃ catalyst represents a composition of a quadrupole doublet and six-line pattern (Table 4). The spectrum,

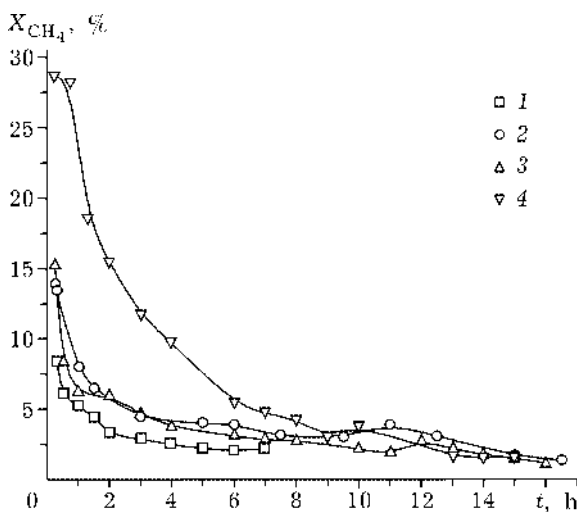


Fig. 2. The global kinetics of methane decomposition on the Fe-Al₂O₃, Fe-Co-Al₂O₃ and Fe-Ni-Al₂O₃ catalysts at 625 °C: 1 – 90Fe-Al₂O₃; 2 – 85Fe-5Co-Al₂O₃; 3 – 85Fe-5Ni-Al₂O₃; 4 – 45Fe-45Ni-Al₂O₃.

TABLE 4

Mössbauer parameter for 85Fe-5Co-Al₂O₃ catalyst (δ is isomer shift, ϵ is quadrupole splitting, H is magnetic field)

Sample	Spectrum	Phase	δ , mm/s	ϵ , mm/s	H , T	Rel area
85Fe-5Co-Al ₂ O ₃ calcined in air at 450 °C	Doublet Six-line pattern	Superparamagnetic Fe ₂ O ₃ Fe ₂ O ₃	0.34±0.01 0.39±0.03	0.86±0.02 -0.12±0.02	51.2±0.07	0.92 0.08
85Fe-5Co-Al ₂ O ₃ reduced in H ₂ at 580 °C	The same	Fe-Co	0.01±0.01	0.00±0.02	34.2±0.02	1.00
85Fe-5Co-Al ₂ O ₃ after 20 min in CH ₄ decomposition at 625 °C	» »	Fe-Co Fe ₃ C	-0.01±0.01 0.20±0.03	0.01±0.01 0.01±0.03	34.5±0.02 20.6±0.05	0.77 0.23
85Fe-5Co-Al ₂ O ₃ post reacted in CH ₄ at 625 °C	» »	Fe-Co Fe ₃ C	0.03±0.01 0.20±0.04	0.00±0.01 0.01±0.04	34.7±0.02 20.5±0.08	0.94 0.06

according to the determined parameters, is characteristic for Fe³⁺, located in a high-spin state and octahedral surrounding of oxygen anions. Accounting for the chemical nature of the precursor and method of preparation of a Fe-Co oxide system it may be assumed that following the proposed method of synthesis the iron oxide is obtained. The presence of the quadrupole doublet and large value of ϵ indicate that it is in highly dispersed, superparamagnetic condition, and the particle size is not more than 80 Å. The similar parameters of the spectra were observed for highly dispersed Fe₂O₃ in the work [20]. The six-line pattern (see Table 4) corresponds to the admixture of the Fe₂O₃ with a rather large size of particles. The fraction of this state is estimated as about 8 % based on the area under the lines.

It is known, that iron can exhibit several crystal structures. α -Fe having a body centered cubic lattice with symmetry $Im\bar{3}m$ exists at the temperatures below 769 °C. α -Fe has ferromagnetic properties. It was established that a bulk

$\alpha \rightarrow \beta$ phase transition occurs at 769 °C. β -Fe has the same symmetry as α -Fe, but already exhibits paramagnetic properties. γ -Fe is formed at the temperatures above 917 °C, and has face centered cubic lattice with $Fm\bar{3}m$ symmetry. Since we work at the temperatures below 700 °C, we should expect formation of only α -Fe, that is confirmed by XRD.

XRD data (Table 5) of reduced catalysts show presence of α -Fe phase in the samples. The traces of Fe-Co-Al spinels are observed for the catalysts containing 10 % mass Al₂O₃. The Mössbauer spectrum of the reduced 85Fe-5Co-Al₂O₃ sample shows a six-line pattern characteristic of Fe-Co alloy plus a central doublet which can be attributed to the traces of superparamagnetic Fe₂O₃. The reduced catalyst represents an alloy Fe-Co. The value of magnetic field exceeds the magnetic field for pure iron and corresponds to the alloy Fe-Co with 5 % mass of Co (see Table 4). According to the TEM data average particle size of the 85Fe-5Co-Al₂O₃, 60Fe-30Co-Al₂O₃, 50Fe-6Co-

TABLE 5

X-ray diffraction and TEM data for the reduced Fe-Al₂O₃ and Fe-Co-Al₂O₃ catalysts

Sample	d , Å	Phase	Particle size (TEM), nm
90Fe-Al ₂ O ₃	2.867	α -Fe, Fe-Al spinel (traces)	35-55
50Fe-Al ₂ O ₃	2.867, 8.242	α -Fe, Fe-Al spinel	30-40
85Fe-5Co-Al ₂ O ₃	2.866	α -Fe, Fe-Co-Al spinel (traces)	25-35
60Fe-30Co-Al ₂ O ₃	2.863	α -Fe, Fe-Co-Al spinel (traces)	25-35
50Fe-6Co-Al ₂ O ₃	2.865, 8.261	α -Fe, Fe-Co-Al spinel	25-35

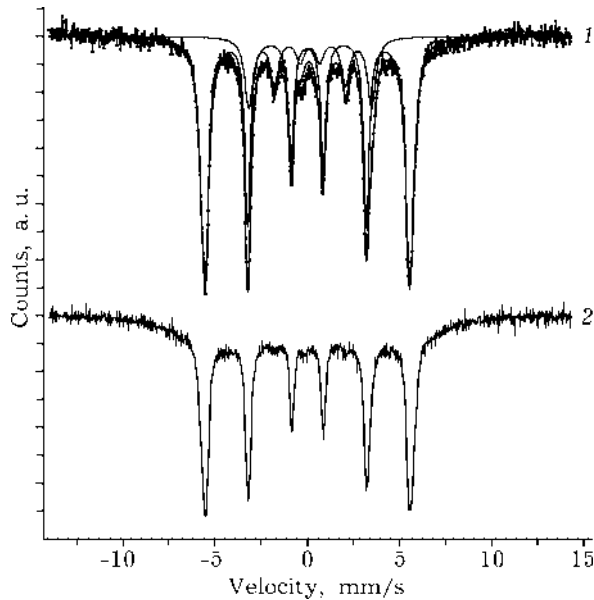


Fig. 3. Mössbauer spectra of ^{85}Fe -5Co- Al_2O_3 catalyst: 1 – after 20 min in methane decomposition reaction at 625°C ; 2 – after 50 min in methane decomposition reaction at 625°C .

Al_2O_3 samples is 25–35 nm, for the $90\text{Fe}-\text{Al}_2\text{O}_3$ – 35–55 nm, in case of the $50\text{Fe}-\text{Al}_2\text{O}_3$ – 30–40 nm.

The Mössbauer spectrum of the catalysts after 20 min in methane decomposition reaction (Fig. 3, curve 1) and after complete deactivation at 625°C consist of superposition two sextets which can be attributed to Fe–Co alloy and Fe_3C . It should be noted that the amount of observed Fe_3C in the deactivated catalyst is essentially less than in the sample after 20 min in methane decomposition. XRD data show also formation of Fe_3C phase.

In the case of the $85\text{Fe}-5\text{Co}-\text{Al}_2\text{O}_3$ sample after 50 min exposition to reaction mixture the Mössbauer spectrum with complicated structure is observed (see Fig. 3, curve 2). There is a “sagging” of the spectrum central part. Probably the formation of metastable [Fe–C] has resulted in appearance of such kind of the spectrum.

Morphology and texture of carbon

TEM images of CFC, formed upon low-temperature methane decomposition over $50\text{Fe}-\text{Al}_2\text{O}_3$, $85\text{Fe}-5\text{Co}-\text{Al}_2\text{O}_3$ and $70\text{Fe}-20\text{Ni}-\text{Al}_2\text{O}_3$ catalysts, are presented in Fig. 4. The formed carbon has filamentary morphology and represents carbon nanotubes, consisting from the

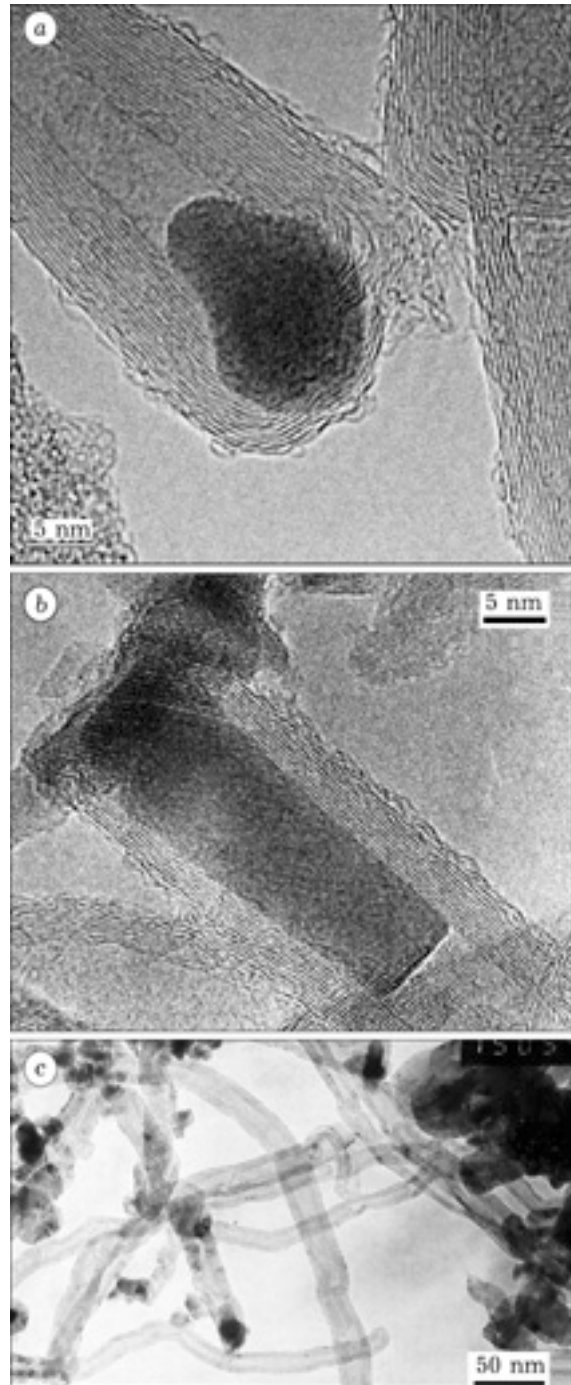


Fig. 4. TEM photographs of the catalysts: a – $50\text{Fe}-\text{Al}_2\text{O}_3$, b – $85\text{Fe}-5\text{Co}-\text{Al}_2\text{O}_3$, c – $70\text{Fe}-20\text{Ni}-\text{Al}_2\text{O}_3$ after 50 min in methane decomposition at 625°C , showing formation of the carbon nanotubes.

turbostratic carbon layers, which are parallel to the fiber axis and look as cylinders with growing diameters enclosed in each other. The turbostratic nature of the formed carbon is confirmed by XRD data (Table 6), indicating that the interplanar distance d_{002} is equal to

TABLE 6

Textural and structural properties of CFC formed in the methane decomposition at 625 °C

Sample	S_{BET} , m ² /g	V_{pore} , cm ³ /g	V_{μ} , cm ³ /g	D_{pore} , Å	d_{002} , nm	L_c , nm
85Fe-5Co-Al ₂ O ₃	103.1	0.4417	0.0046	171	0.342	6.5
80Fe-10Co-Al ₂ O ₃	118.2	0.3737	0.0057	126	–	–
60Fe-30Co-Al ₂ O ₃	136.0	0.4744	0.0047	149	0.340	11.0
50Fe-Al ₂ O ₃	151.5	0.5006	0.0068	132	0.343	8.7
50Fe-6Co-Al ₂ O ₃	155	0.5582	0.0101	144	0.342	8.2
80Fe-10Ni-Al ₂ O ₃	139.1	0.4871	0.0070	140	–	–
70Fe-20Ni-Al ₂ O ₃	121.1	0.5481	0.0073	188.6	–	–

0.343 nm, *i. e.* a little higher than in a perfect graphite ($d_{002} = 0.335$ nm), and also by HRTEM data (see Fig. 4, *a*, *b*). The diameter of carbon nanotubes varies at the range of 30–50 nm.

The analysis of TEM data allows to pick out two types of filamentous carbon. Type I is nanotubes, consisting from 7–15 graphitic cylindrical layers, with outer diameter ranging between 25–30 nm and inner channel of 10 nm (see Fig. 4, *b*). Type II is carbon fibers, which have internal caps formed by linkage of the inner carbon layers are observed. All of the internal caps are oriented perpendicularly to the fiber axis and along one direction only for the given fibers. Carbon fibers are observed predominantly in CFC (50Fe-Al₂O₃) and to a lesser extent in CFC (85Fe-5Co-Al₂O₃).

Nanotubes (type I) are formed mainly upon methane decomposition over 85Fe-5Co-Al₂O₃, however their yield does not exceed 20 g/g_{cat}. The carbon capacity is increased up to 52.4 g/g_{cat} with a diminution of the iron contents in the catalyst down to 50 % mass (catalyst 50Fe-6Co-Al₂O₃), however in this case carbon fibers (type II) are formed.

An increase of the Ni content in the Fe–Ni catalysts up to 70 % mass formation of CFC characteristic for CFC (90 % mass Ni-Al₂O₃) is observed. The catalytic particles have cubooctahedral shape, the carbon filament consists from graphitic planes which are coaxially arranged as cones at the angle 45° [10].

Textural properties of the tubular formed carbon were determined by nitrogen adsorption at 77 K (see Table 6). The magnitude of specific surface area (S_{BET}) varies in the range of 100–150 m²/g. The tubular CFC is more friable on the packing with a bulk density of

0.2 g/cm³, pore volume of 0.5 cm³/g and average pore diameter of 15 nm. Interplanar distance d_{002} and the average size of the coherent scattering area directed perpendicular to the graphite plane (002) (L_c) of CFC were determined from XRD data and represented in Table 6.

The nature of iron-containing catalyst promotion

It is known, that carbon deposition deactivates the catalyst in hydrocarbon decomposition reactions at high temperatures. However hydrocarbon decomposition under certain conditions, may result in the formation of filamentous carbon which does not poison the catalyst for a long time. Data presented above, show that it is possible to create long-living iron catalysts of methane decomposition if the conditions of filamentous carbon growth are ensured.

The properties of Fe-containing catalysts are found to be similar to the properties of Co-containing catalysts, and depend on the preparation method, amounts of the metal and temperature regimes [11]. Among the investigated catalysts, the best properties are exhibited by coprecipitated Fe-Al₂O₃ using aqueous solution of NH₄OH as a precipitant and containing not less than 50 % mass of Fe (see Table 1). Brown *et al.* [21] had established, that introduction of Co at the stage of Fe and Al hydroxides formation results in the decrease of reducing temperature of iron oxides. Indeed, the known iron Fischer–Tropsch catalysts and catalysts for ammonia synthesis are reduced at the temperatures below 600 °C. We have found, that the most effective Fe-Al₂O₃

catalysts of methane decomposition are formed after reduction at the temperature of 580 °C, with subsequent passivation at room temperature in ethanol.

We have determined, that the maximum growth of filamentous carbon on Fe-Al₂O₃ catalysts occurs at 625 °C. Thus, the temperature at which iron-containing catalysts show considerable efficiency in CFC deposition is much below than it was found in the works [15, 16]. It is known that the high-loaded metal catalysts have the greatest activity in low-temperature methane decomposition and CFC formation. However, the carbon capacity of pure iron catalysts was small, that can be explained by the low contents of iron metal, which is a center of carbon deposition, and the maximum carbon yield is observed for the sample with 50–80 % mass Fe. Apparently the increase of high-to-reduce oxide admixture (Al₂O₃) in the catalyst results in the formation of the iron particles having appropriate size (≈25–35 nm) to growth of carbon filament.

We have shown, that introduction of the small amounts of cobalt (3–10 % mass) in Fe-Al₂O₃ catalysts at the stage of coprecipitation increases CFC yields 2–3 times (see Table 2, Fig. 1, b). The carbon capacities presented in Fig. 1, b show that iron is less active than Fe-Co or Fe-Ni alloys. But the curves of the carbon capacity dependence for Fe-Co and Fe-Ni on the second metal loading (Co, Ni) differ from each other. The carbon capacity dependence for Fe-Co has a brightly expressed maximum at 10–20 % mass Co, while for Fe-Ni extremum is not observed. There is, however, a significant decrease in the carbon yield for Fe-Co catalysts with increase of the Co content. This catalytic behavior is connected to the fact that pure cobalt is active in methane decomposition reaction at 500 °C, and inactive at 625 °C due to sintering of catalytic particles. Our results show that an increase in the Ni content of the Fe-Ni catalysts from 5 to 40 % mass is accompanied by an increase in the amount of deposited carbon from 12 to 22 g/g_{cat}. Further addition of Ni appeared to exert very little impact on the carbon yield and catalyst properties become similar to that exhibited by 90 % mass Ni-Al₂O₃ under the same condition, that is expressed in the increase of methane con-

version and the modification of the CFC characteristics. The Fe-Co catalysts containing 5–10 % mass of Co are some effective in nanotube formation than Fe-Ni alloys, *i. e.* the promotion influence of the small amount of Co is more expressed than in case of Ni.

Taylor *et al.* [19] had established that some cobalt (5 % mass) or nickel (5–15 % mass) has a beneficial influence on iron for nitrogen adsorption, synthesis of ammonia and isotope exchange ¹⁴N₂–¹⁵N₂. They assumed [19], that the small amounts of Co or Ni affect the crystallisation of iron such that a greater proportion of the surface area exists as (111) faces, which are particularly active in the synthesis of ammonia and adsorption of N₂ [22], and these faces are necessary for the deposition of graphitic carbon upon hydrocarbon decomposition.

The typical global kinetics of the methane decomposition over Fe-Al₂O₃ is illustrated in Fig. 2. There is no induction period for Fe-Al₂O₃ catalysts, which is characteristic for Ni-Al₂O₃. Previously we have assigned the induction period to the sintering of carbon-saturated Ni particles from 17 to 50 nm within the first minutes of reaction [10]. The Fe-Al₂O₃ (Fe-Co-Al₂O₃) active particle size is 20–35 nm, which seems to be large enough for filamentous carbon growth. Based from the kinetics of methane conversion, it is possible to explain gradual fall of catalyst activity due to a covering of the active centers by constantly generating carbon nanotubes, so-called encapsulation of the active centers.

Fig. 4, a–c demonstrate the active centers of iron-containing catalysts of methane decomposition. On the basis of the TEM data it can be assumed that the formation of graphite phase at initial stage of methane decomposition reaction leads to generation of faceted catalyst crystallites – the carbon nanotube growth centers apparently only at addition of the second metal (Co or Ni). Conventional model of methane decomposition includes the following stages: decomposition of CH₄ on the metal (100) and (110) planes involving the formation of surface carbon; carbon diffusion through a metal particle, and graphite precipitation on the metal (111) planes [8].

The Co addition is likely to cause the formation of catalyst particles with allocation of

(100) planes where methane decomposition occurs, and planes (111) where carbon deposition can take place. Due to the certain orientation of the catalyst particle when the plane (100) is located perpendicularly to the carbon fiber growth direction the formation of carbon nanotubes with hollow internal channel is provided. Thus iron catalyst promotion by Co or Ni changes the shape of the active particles and the mechanism of the carbon deposition.

CONCLUSION

Fe-Al₂O₃, Fe-Co-Al₂O₃ and Fe-Ni-Al₂O₃ catalysts have sufficient efficiency in filamentous carbon formation and in a methane decomposition at moderate temperature (625 °C). It has been established, that the properties of Fe-containing catalysts depend on a preparation method. The best method is a coprecipitation of components from solutions of appropriate metal nitrates by a solution of ammonia (Fe-Co-Al₂O₃) or ammonia bicarbonate (Fe-Ni-Al₂O₃). Carbon capacity of Fe-Al₂O₃ catalysts is increased in the presence of Co or Ni and reaches 52.4 g/g_{cat} (104 g/g_{Fe}). TEM data have shown, that the carbon nanotubes are observed upon methane decomposition on the Fe-Co(Ni)-Al₂O₃ catalyst. Application of the developed catalysts allows to obtain CFC with a new microstructure (carbon nanotubes), which now have scientific and practical interest.

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