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Stages of Filamentary Carbon Growth from Hydrocarbons on Nickel-containing Catalysts and Causes of their Deactivation

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Abstract

Methane decomposition to carbon and hydrogen has been studied using the Ni/Al_2O_3, Ni-Cu/Al_2O_3 and Ni-Cu/MgO catalysts at 550°C. The S-shaped kinetic curves of carbon formation from methane exhibit the following periods: induction, acceleration, stationary state and deactivation. The induction period is characterized by oversaturation of metal or alloy particles with carbon atoms and predominant formation of the graphite phase at the (111) faces of the catalyst particles. After formation of the graphite crystallization centers, the acceleration period is accompanied by the growth of graphite filaments and simultaneous reconstruction of the metal particles. After termination of the above processes, the carbon deposition rate becomes constant. Deactivation of the catalyst is caused by blocking of the front side of the metal particle with a carbon film. When the reaction temperature increases to 700°C, deactivation of the nickel-containing catalyst follows a different mechanism. During the growth of the filamentary carbon, the metal particle becomes viscous-flowing. This fact allows for its partial capturing by the inner filament channel. As a result, the formed carbon filament has an internal channel filled either with metal or its alloy. Hydrogen addition to methane leads a decrease in the carbon formation rate on the catalyst and a change in the filamentary carbon morphology: now it contains a hollow channel.

Introduction

The formation of carbon nanofibers with different crystallographic, morphological, textural and other properties is among the most intensively studied areas in the last few years [1,2]. At present, considerable progress has been made in studying the mechanism of the filamentary carbon growth [3]. It has been established that iron subgroup metal particles 50-1000 Å in diameter initiate the growth of filamentary carbon [3-6]. During this process, hydrocarbons decompose to yield carbon atoms at the front faces of the metal particles. Then, carbon atoms diffuses through the particle volume to the rare faces to form various graphitic structures. The growth of filamentary carbon involves induction, acceleration, stationary and deactivation periods. The induction and acceleration periods are observed at the beginning of the filamentary carbon growth. During the following stationary period the rate of filamentary carbon growth is constant. Then, the process stops.

The stationary period of the filamentary carbon growth has been studied most thoroughly. A metal crystal formed at the end of a filament has certain orientation with respect to the filament axis. For nickel particles, the (100) crystallographic direction coincides with the filament axis. Diffusion of carbon atoms through the nickel monocrystal is the limiting stage in the filamentary carbon growth. The driving force for the carbon diffusion through the nickel crystal logically follows from the carbide-cycle mechanism [1,3,7,8]. The carbon concentration at the (100) and (110) faces of the front crystal side is close to that in nickel carbide Ni_3C. The carbon concentration at the (111) faces of the rare particle side, where the graphite layer growth takes place, is equal to the concentration of saturated carbon solution in nickel. Carbon diffuses through the nickel crystal due to the presence of a concentration gradient.

In this work we focus on the study of the initial and final stages of the filamentary carbon growth and transformations of this process with reaction temperature. In a number of cases, a hollow channel was formed in the central part of a carbon filament [2,9-13]. Since the reasons for its formation are still unclear, we would like to dwell on this problem.

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Experimental

The formation of different morphological carbon structures from hydrocarbons was studied on the Ni/Al_2O_3 catalyst (nickel concentration 85 wt.%) and nickel-copper alloys supported on the aluminum and magnesium oxides (75%Ni–12.5%Cu/Al_2O_3 and 75% Ni–12.5%Cu/MgO). The support weight was 12.5% of the catalyst weight. The catalyst samples were prepared by mechanical activation of oxide and hydroxide metal powders. It takes high energy density in the working area to provide efficient mechanochemical activation of a solid. For this reason, we used planetary centrifugal mills. Two modifications of the 85%Ni/Al_2O_3 catalyst were prepared by 5 and 30 min activation.

The kinetics of the carbon formation from methane was studied using a flow quartz reactor with a spring balance under no gradient conditions with respect to temperature [14]. The catalyst sample weight was 0.002–0.5 g, the balance sensitivity was 1×10^{-4} g. Methane and argon were of 99.92 and 99.97 vol.% purity grade, respectively. The nickel-containing catalysts were reduced by heating to 550°C in a hydrogen flow for 20-30 min. Prior to their contact with air, the reduced catalysts were deactivated at room temperature by treatment under argon flow (80 L/h Ar) fed with oxygen pulses (3 L/h oxygen).

X-ray diffraction (XRD) patterns of the samples were recorded using a Siemens D-500 diffractometer with Cu K_α radiation (a graphite monochromator on the reflected beam).

The carbonized catalysts were studied by transmission electron microscopy using a JEM-100CX electron microscope (accelerating voltage 100 kV, spherical aberration coefficient of the objective lens 2.8 mm, resolution to lines 2 Å).

Results and Discussion

Figure 1 shows kinetic curve of carbon formation from methane on the 85 wt.% Ni/Al_2O_3 catalyst subjected to mechanical activation at 550°C for 5 min. Most of carbon exists as nanofibers. The curves suggest four different periods in the formation of carbon that are primarily associated with peculiarities of the filamentary carbon growth. The formation of filamentary carbon is known to be initiated by nickel particles 50-1000 Å in diameter. In order to find the reason for existence of different periods in the filamentary carbon growth, we studied changes in the shape of nickel particles during the growth of filamentary carbon. For this purpose, 85%Ni/Al_2O_3 catalyst samples were carbonized for different times. The obtained samples with different carbon concentrations (92; 330 and 900% relative to the catalyst weight) and the initial catalyst were investigated by XRD and electron microscopy.

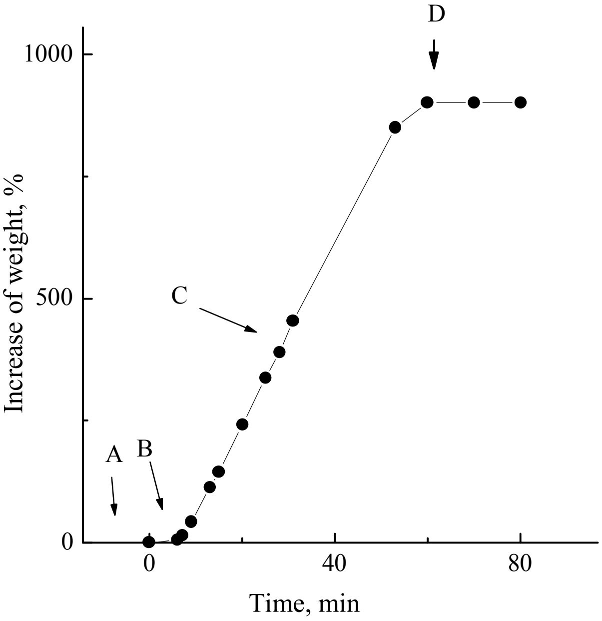

Fig. 1. Formation of carbon from methane on the Ni/Al_2O_3 catalyst at 550°C (activation time is 5 min).

After reduction of the nickel-alumina catalyst, crystalline nickel particles of different shapes begin to form. Data on the X-ray phase analysis of the regions of coherent scattering and parameter of the nickel crystal lattice are given in Table 1. As follows from the table, the growth of filamentary carbon insignificantly increases the nickel lattice parameter, which we attribute to the formation of a saturated solution of carbon in nickel. According to the carbide cycle mechanism, an unstable carbide-like state /Ni-C/, resulting from decomposition of the hydrocarbon, decomposes into carbon and the metal. At temperatures higher than 400°C, a nickel carbide phase does not form, because the rate of its formation is lower than that of decomposition. As the reaction temperature is decreased below 400°C, the relation between the rates of formation and decomposition of the nickel carbide phase becomes opposite, which results in the formation of nickel carbide, Ni_3C.

The "carbide cycle mechanism" suggests that during the induction period of the filament growth carbon atoms resulting from methane decomposition dif-

Table 1
Data on X-Ray phase analysis of the 85%Ni/Al_2O_3 catalyst containing different amounts of carbon

Sample number	Carbon concentration, mass.%	Diameter of Ni crystallites, Å	Parameter of Ni lattice, Å
1	0	160	3.5242
2	92	160	3.5246
3	330	150	3.5265
4	900	120	3.5265

fuse to the bulk of the metal to form an oversaturated solution of carbon in nickel. Considerable oversaturation of nickel with carbon is associated with the fact that nucleation of the graphite phase calls for overcoming of a high potential barrier. For this reason, the concentration of carbon dissolved in nickel increases during the initial stage of hydrocarbon decomposition.

When the critical oversaturation degree is reached and a crystal graphite nucleus is formed at some place, carbon atoms rapidly move here until a saturated solution is attained. The graphite-phase nuclei prefer to form at the nickel faces (111) because the symmetry and parameters of flat nickel (111) and graphite (002) lattices agree very well.

The appearance of graphite crystallization sites is followed by growth of graphite filaments and simultaneous reconstruction of the metal particle structure. This is a labile, viscous-flowing but still solid system. This observation is confirmed by the agreement between the activation energy of the filamentary carbon growth (diffusion of carbon atoms through the nickel crystal is known to be the rate determining stage) and tabular data on the activation energy of carbon diffusion in nickel metal. During this time, the carbon formation is accelerated to attain a stationary mode.

As follows from Table 1, the size of nickel crystals reduces from 160 to 120 Å due to the growth of filamentary carbon. This decrease can be caused by two reasons: (a) nickel atoms are removed into a carbon filament (b) an intensive flow of carbon atoms through a nickel crystal induces the accumulation of defects and then provides a separation of monocrystals into units. Since the presence of nickel atoms was not observed in the body of carbon filament, the second reason is more probable.

Earlier we suggested that shaping of the metal particle crystal depends on the evolution intensity and mass transfer of carbon atoms as well as formation of a graphite structure [3]. The more intense is this process, the more labile is the structure of the metal particle.

For instance, on Ni-Cu alloys such process results in the formation of "octopus"- like carbon deposits [5,6,15,16]. In this case, one particle of the nickel-copper alloy initiates the growth of several filaments in different directions (Fig. 2a). For nickel metal [5], the rate of carbon emission is 2-3 times higher than that on the Ni-Cu alloy. Therefore, the graphite layers formed at different nickel faces start aggregating (Fig. 2b). Then, during the growth of new graphite layers, a nickel particle moves up, whereas the (111) nickel face and the (002) basal graphite face slide relative to each other. Every new plate of graphite slides down to the central part of the filamentary carbon. High mobility of nickel atoms at the Ni-C interface leads to a shift of the nickel surface atoms to the filament axis. This accounts for a significant transformation of the metal particle during the acceleration period of the carbon formation rate. In this case, the nickel particle shape shown in Fig. 2b transforms into the one presented in Fig. 2c. Figure 3 shows that nickel particles initiating the growth of filamentary carbon from methane on the Ni/Al_2O_3 catalyst are nicely cut. The (100) face is directed towards the growth direction, whereas the tail part of the nickel crystal is formed by (111) faces. These faces form a pyramid with a vertex oriented in the direction opposite to that of the filament growth.

Hence, it is clear that after the induction period the formation of new crystallization sites on any areas of the metal particle surface is practically impossible. As a result, the part of the metal particle where the formation of a graphite phase starts becomes the back side of the particle where a graphite filament grows. All other faces that are not shielded with graphite begin to act as a "front" side where methane decomposes via the carbide cycle mechanism. At relatively low temperatures (475-525°C) such nickel crystal shape remains unchanged for a long period of time providing stable growth of filamentary carbon. This is characteristic of the stationary period of the filamentary carbon growth. Fig. 3 shows an electron micrograph of the filamentary carbon formed on the 85%Ni/Al_2O_3 catalyst at 550°C. The concentration of carbon in the sample is 92 wt.% relative to the catalyst weight. According to the crystallographic data, the angle α between the (111) edges should be

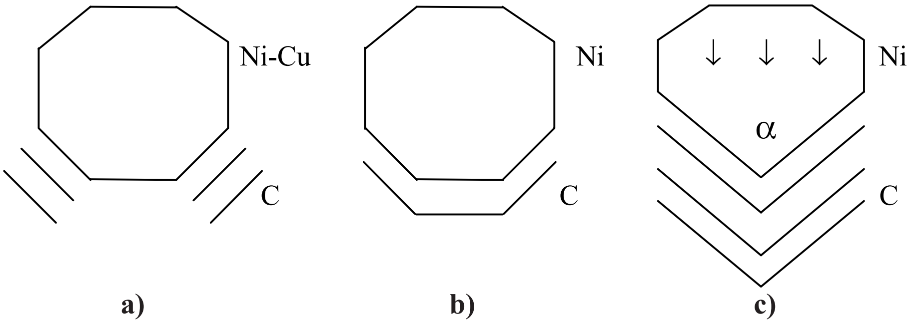

Fig. 2. Schematic diagram of the mechanism of the filamentary carbon nucleation and growth on Ni and Ni-Cu crystals.

ca. 71°. However, at 550°C the removal of nickel to the "tail" part of the crystal is rather active resulting in a decrease of α to 50-60° (Fig. 3). We suggest that the relief of these faces is formed by atomic steps that change the plate inclination.

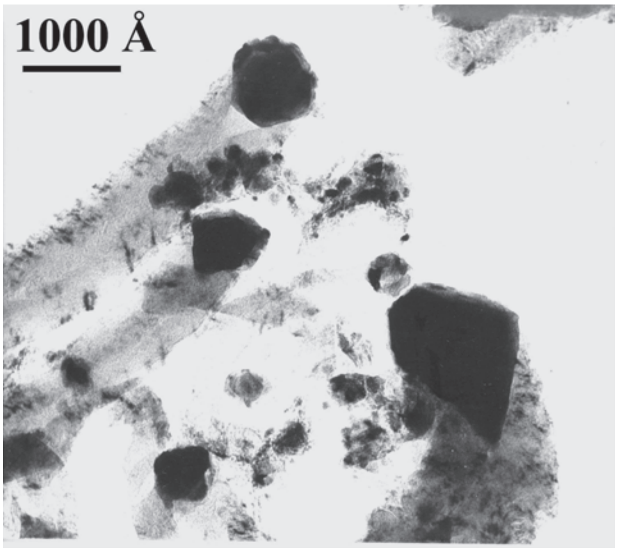

Fig. 3. Micrograph of the filamentary carbon formed from methane on the 85%Ni/Al_2O_3 catalyst at 550°C (the carbon concentration in the sample is 92 wt.% relative to the catalyst weight).

The question arises of whether there are differences in the shape of a metal particle, observed during the growth of filamentary carbon and that after completion of the process and removal of the sample from the reactor. It should be noted that the structure and shape of the particle undergo evolution due to intense diffusion of carbon atoms through a metal particle from a frontal to the back surface. This is responsible for lability, viscous fluidity of the metal particles during the growth of filamentary carbon. Due to high mobility of the structure elements of the metal particles, they adopt a definite shape which is epitaxially rigidly bound to the structure of the growing fibers. Lability and viscous fluidity vanish as the filaments stop to grow. The particle "freezes" in its state. It cannot change its shape due to rigid epitaxial dependence on the stable carbon fiber structure.

Cooling of the sample to room temperature with following heating to 550°C do not affect the kinetics of formation of carbon fibers.

Causes of alumina-nickel catalyst deactivation during nucleation of filamentary carbon

An electron microscopy study of deactivated 85% Ni/Al_2O_3 catalyst having 900% of deposited carbon relative to the catalyst weight showed that the front side of nickel particles is covered with a carbon film (Fig. 4). As already mentioned above, carbon atoms diffuse through the nickel particle under the density gradient action. The concentration of carbon at (100) and (110) faces of the front crystal side exceeds the equilibrium concentration on the nickel-graphite interface. In this situation, a significant role is played by the relation between the hydrocarbon decomposition rate (*i.e.* rate of atomic carbon formation at the front side) and the rate of diffusive mass-transfer of carbon from the places of its formation. When this relation reaches a certain critical value, conditions required for condensation of atomic carbon as an independent phase are met. This results in coating of the front particle side with carbon.

We believe that considerable oversaturation of the subsurface zone of the metal phase with carbon and constant surface chemical processes (the carbide cycle) resulting in the carbon accumulation, favor surface reconstruction of the metal particle front face involving the appearance of steps typical for faces (111). This phenomenon also initiates the formation of a graphite film that coats the front face of the metal particle.

It is important to note that as soon as an individual graphite phase appears at the front side of a metal

Fig. 4. Micrograph of the filamentary carbon formed from methane on the 85%Ni/Al_2O_3 catalyst at 550°C (the carbon concentration in the sample is 900 wt.% relative to the catalyst weight).

particle, the gradient of carbon concentration in the metal particles that provides the carbon transportation to the growing nanofibers disappears and the nanofibers stop growing. This is the phenomenon leading to the catalyst deactivation. In several cases, a nickel particle situated at the end of a no-longer growing carbon fiber regains its spherical shape. The absence of a directed diffusion flux through the nickel crystal and a tendency of the particle to attain configuration with the minimal Gibbs excess surface energy are responsible for reverse reconstruction of metal particles.

Effect of the reaction temperature on the mechanism of the filamentary carbon growth from methane on nickel-copper catalysts

An increase in the reaction temperature affects the features of filamentary carbon growth both on nickel and nickel-copper catalysts. At higher temperatures deactivation of the filamentary carbon follows the second mechanism. The kinetic curves of carbon formation from methane at different temperatures on the Ni/Al_2O_3 and Ni-Cu/MgO catalysts are shown in Figs. 5 and 6, respectively. Both figures suggest that the initial rate of carbon formation increases with growing temperature. Note that as temperature increases to 700°C, the high rate of carbon formation is observed only for several minutes (initial part). Then, it rapidly drops.

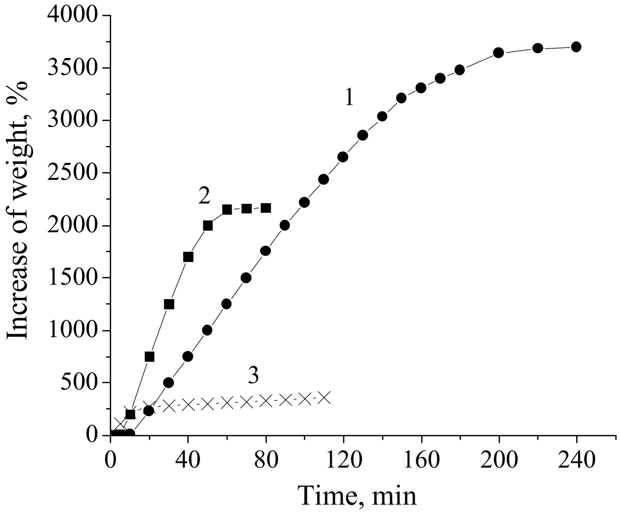

Fig. 5. Formation of carbon from methane on the Ni/MgO catalyst (activation time is 30 min) at 550°C (1), 600°C (2) and 700°C (3).

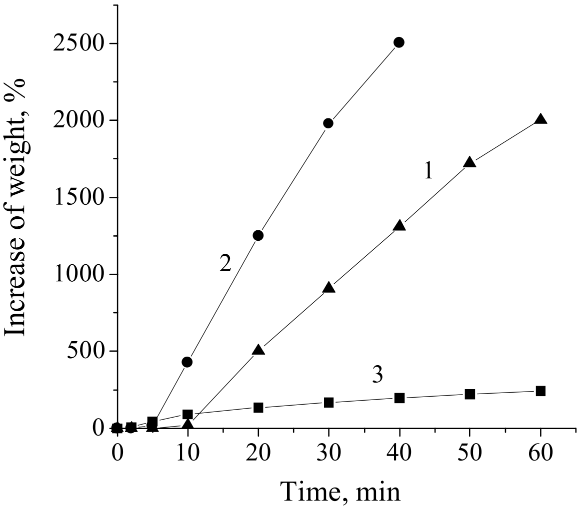

Fig. 6. Formation of carbon from methane on the 75%Ni – 12.5%Cu/MgO catalyst at 550°C (1), 600°C (2) and 700°C (3).

Figure 7 shows a micrograph of the filamentary carbon formed at 750°C on the Ni/Al_2O_3 catalyst. One can clearly see that as the filamentary carbon grows, the nickel particle expands along the filament length. As a result, the filament acquires an inside channel filled with nickel. The filamentary carbon formed on the Ni-Cu/MgO catalyst at 700-750°C has a similar morphology. Here we can see another reason for deactivation of the metal particle. In this case, the particle where the filament grows is encapsulated by the filament. A natural question is: What process is responsible for the formation of an inner cavity in the graphite filament and what forces spread the metal particle over this cavity?

We found that an increase of the process temperature and the graphite filament growth rate results in the increase of the viscous fluidity of the metal particle and fast removal of nickel atoms towards the diffusion flux of carbon atoms (*i.e.* to the tail part of the metal particle). As a result, the particle becomes longer, and α decreases considerably. The catalytic particle transforms from the state shown in Fig. 8a into the state shown in Fig. 8b.

Fig. 7. Micrograph of the filamentary carbon formed from methane on the 85%Ni/Al_2O_3 catalyst at 750°C.

The situation is different when carbonization is carried out in the methane-hydrogen medium (CH_4:H_2 = 1:1) at 700°C. Then, the morphology of the filamentary carbon formed on the Ni/Al_2O_3 and Ni-Cu/MgO catalysts changes (Figs. 9, 10). The filamentary carbon formed on the both catalysts contains a hollow channel.

We have already noted that intensification of this process increases the probability of the metal particle rearrangement and even disappearance of some faces and development of other ones. In this case, hydrogen addition to methane initiates methanation of carbon atoms at the front side. To put it differently, the observed reaction is the reverse of the methane decomposition, the concentration of carbon atoms at the front side decreases, and the whole process slows down. A decrease in both formation intensity and concentration of carbon atoms at the front part is responsible for a decrease in the carbon concentration gradient between the front and rare sides and a change in the diffusion mass transfer of carbon to the rare side. As a result, most of carbon has time to deposit on less distant parts denoted with arrows in Fig. 8c. Since a carbon flow to more distant parts of the rare surface becomes weaker, reverse rebuilding and reforming of face (100) can occur there. Though carbon will also deposit on this face, its deposition rate will be much lower. As a nanofiber grows, a metal particle is continuously forced out of its body. As a result, the particle leaves the filament to yield a hollow channel. As follows from the micrograph (Fig. 10), graphite layers slowly formed at the (100) face undergo periodical detachment as partitions in the hollow channel.

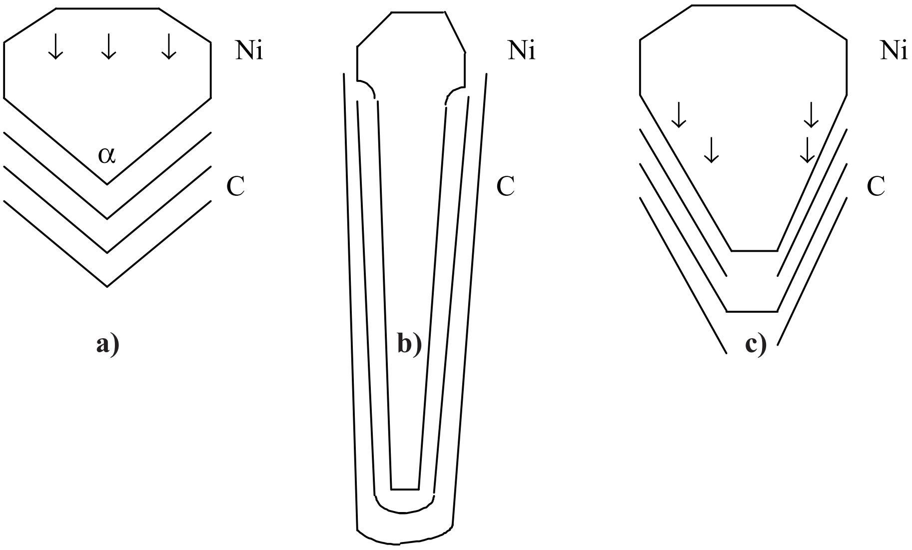

Fig. 8. Transformation of catalytic particles during the reaction temperature increase from 500 to 700-750°C.

Fig. 9. Micrograph of the filamentary carbon formed from methane diluted with hydrogen (CH_4:H_2 = 1:1) on the 85% Ni/Al_2O_3 catalyst at 700°C.

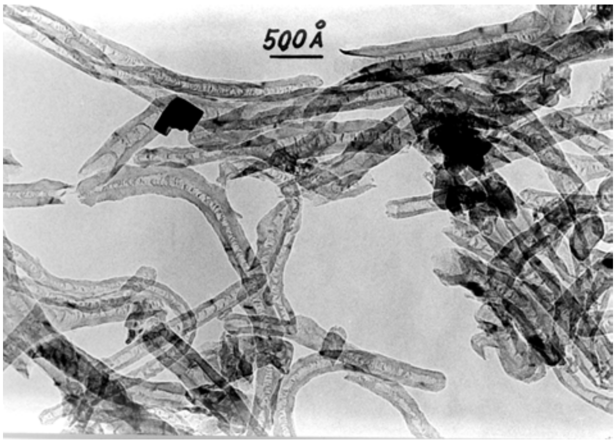

Fig. 10. Micrograph of the filamentary carbon formed from methane diluted with hydrogen (CH_4:H_2 = 1:1) on the 75%Ni – 12.5% Cu/Al_2O_3 catalyst at 700°C.

Conclusions

Methane decomposition to carbon and hydrogen has been studied using the 85%Ni/Al_2O_3, 75%Ni-12.5%Cu/Al_2O_3 and 75%Ni-12.5%Cu/MgO catalysts at 550°C. The S-shaped kinetic curves of carbon formation from methane exhibit the following periods: induction, acceleration, stationary state and deactivation. The induction period is characterized by oversaturation of metal or alloy particles with carbon atoms and predominant formation of the graphite phase at the (111) faces of the catalyst particles. After formation of the graphite crystallization centers, the acceleration period is accompanied by the growth of graphite filaments and simultaneous reconstruction of the metal particles. After termination of the above processes, the carbon deposition rate becomes constant. Deactivation of the catalyst is caused by blocking of the front side of the metal particle with a carbon film. When the reaction temperature increases to 700°C, deactivation of the nickel-containing catalyst follows a different mechanism. During the growth of the filamentary carbon, the metal particle becomes viscous-flowing. This fact allows for its partial capturing by the inner filament channel. As a result, the formed carbon filament has an internal channel filled either with metal or its alloy. Hydrogen addition to methane leads a decrease in the carbon formation rate on the catalyst and a change in the filamentary carbon morphology: now it contains a hollow channel. Thus, the "carbide cycle" mechanism allowed us to describe all stages of the filamentary carbon formation.

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