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Catalyst and Technology for Production of Carbon Nanotubes

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Abstract—Modifying the iron–aluminum catalyst with molybdenum oxide affords a marked increase in the yield of carbon nanotubes from 1,3-butadiene diluted with hydrogen. The optimum catalyst composition is 6.5% MoO_3–52% Fe_2O_3–Al_2O_3. With this catalyst, it is possible to obtain over 100 g of carbon nanotubes per gram of catalyst in a reactor fitted with a McBain balance. Replacing expensive 1,3-butadiene with the cheaper commercial propane–butane mixture (80 mol % propane + 20 mol % butane) leads to a sharp decrease in the nanotube yield because of the lower reactivity of the latter. Based on the concept of the catalytic decomposition of hydrocarbons and the formation of nanosized carbon materials via the carbide cycle mechanism, a new, efficient, CoO–MoO_3–Fe_2O_3–Al_2O_3 catalyst has been developed. The enhancement of the activity of the MoO_3–Fe_2O_3–Al_2O_3 catalyst by promoting it with cobalt oxide is achieved without a change in the rate-limiting step of the process. The design of a continuous reactor for carbon nanotube synthesis is suggested. The characteristics of the resulting nanotubes are presented.

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Nanosized carbon materials (filaments, fibers, tubes, etc.) possess a wide variety of valuable properties [1, 2]. They have firmly occupied their niche in materials science and technology [3, 4]. At present, researchers extensively seek new ways of synthesizing these materials on larger scales adequate to the practical demand.

The latest experience has demonstrated that the catalytic method of carbon nanonaterial synthesis is the most promising. It offers a number of technological advantages over the other known methods, such as the high-temperature sublimation of graphite followed by its deposition.

A significant advantage of the catalytic method is that it offers wide opportunities in selecting process conditions for obtaining materials with the preset properties. We have discovered and thoroughly studied the carbide cycle mechanism of the catalytic formation of carbon nanomaterials [4, 5]. This mechanism provides a means to control the synthesis by varying the process temperature, the nature of the hydrocarbon to be decomposed, the degree of dilution of the hydrocarbon with other gases, the composition and particle size of the catalyst, and other conditions in order to obtain a nanomaterial with the desired characteristics. Earlier, we reported our studies on the technology of preparing carbon nanomaterials with coaxial conical and stacked base crystallographic structures [6].

Here, we report a more efficient catalyst and synthesis conditions for carbon nanotubes with a narrow diameter distribution and the production of this product in a continuous pilot plant with a rotating reactor.

In order to accomplish these goals, it was necessary to solve the following problems:

(1) It was necessary to optimize the catalyst composition and process conditions so as to obtain, with high selectivity and productivity, carbon nanotubes via the decomposition of the commercial propane–butane mixture as the cheapest possible raw material.

(2) Another problem was to form (synthesize) a catalyst with a monodisperse structure and the minimum possible particle size. This would ensure the growth of carbon nanotubes with the smallest and uniform (calibrated) diameter [7, 8].

(3) It was necessary to optimize the process conditions for obtaining the longest possible nanotubes [7, 8].

(4) Finally, it was necessary to improve the design of our old rotating batch reactor [6] so as to make possible its continuous operation.

GENERAL CONCEPTION OF THE PROCESS AND INITIAL INFORMATION

The above problems can be made much easier to solve by using the concept of the carbide cycle mechanism of the formation of nanosized carbon products. For a better understanding of the reasoning presented below, we will briefly recall the basic features of the carbide cycle mechanism of the formation of nanosized carbon materials [4, 5]. This mechanism consists of several steps. The hydrocarbon adsorbs mainly onto the [100] and [110] faces on one side of a catalytic particle. This side of the catalytic particle is called frontal. On this side of the catalytic nanoparticle, the hydro-

carbon decomposes to yield an unstable, intermediate, carbide-like compound. In turn, this compound decomposes to release carbon atoms. These carbon atoms diffuse through the bulk of the catalyst particle to its opposite, rear side. There, a nucleus of a new carbon phase appears on the [111] face, giving rise to the growth of this carbon phase, which can have various morphological and crystallographic properties.

Our earlier studies [4, 5, 9] demonstrated that tubular (coaxial cylindrical) nanosized carbon structures form mainly on fine catalyst particles containing iron. In order to prevent the agglomeration of these particles and enhance the stability of the structure as a whole, aluminum oxide as a stabilizer is introduced into the catalyst.

The diameter of carbon nanotubes is determined by the particle size of the catalyst on which they are grown [8]. Therefore, for obtaining nanotubes with the smallest possible, calibrated diameter, it is necessary to synthesize a catalyst with a monodisperse structure and the minimum possible particle size.

Modification of iron-group metals with molybdenum favors the formation of a monodisperse structure with a small size of catalyst particles [10–13]. This made it possible to obtain carbon nanotubes with a narrow diameter distribution. The preparation of MoO_3–Fe_2O_3–Al_2O_3 catalysts by coprecipitation and their phase composition were described in detail [13].

Modifying the aluminum–iron catalyst with molybdenum oxide yields a hematite-based solid solution in which part of the iron ions is replaced by aluminum and molybdenum ions. Under the action of the reaction mixture at 700°C, the hematite-based solid solution undergoes reduction first to magnetite and then to a Fe–Mo alloy. Molybdenum oxide causes marked changes in the properties shown by the aluminum–iron catalyst in carbon nanotube growth. The nanotube yield passes through a maximum as the molybdenum content of the aluminum–iron catalyst is raised. The optimum catalyst composition is 6.5% MoO_3 + 52% Fe_2O_3 + Al_2O_3.

With this catalyst under the above conditions in a reactor fitted with a McBain balance, we were able to obtain 130 g of carbon nanotubes per gram of catalyst.

However, 1,3-butadiene is economically nonoptimal as a precursor for commercial-scale production of carbon nanotubes. A cheaper raw material is the commercial propane–butane mixture (80 mol % propane + 20 mol % butane). Preliminary experiments demonstrated that use of the propane–butane mixture leads to a much lower nanotube yield because of the lower reactivity of this mixture (Fig. 1). To change to this precursor, it was necessary to raise the activity of the catalyst.

In the work reported here, we used the MoO_3–Fe_2O_3–Al_2O_3 catalyst as the base and studied the effect of another iron-group promoter (Co or Ni) on the hydrocarbon decomposition rate and catalyst productivity.

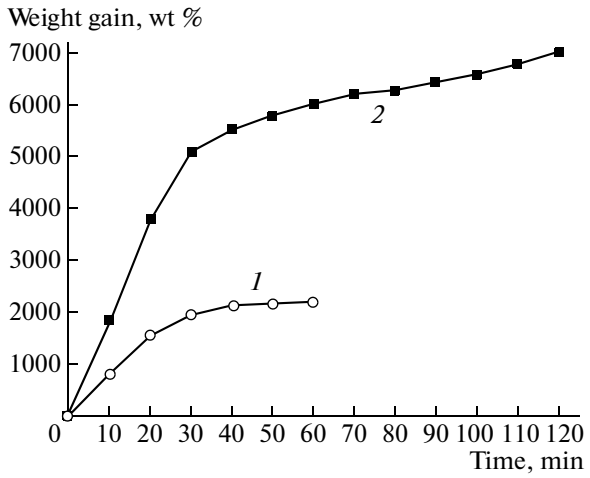

Fig. 1. Kinetics of carbon nanotube formation on the 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalyst at 700°C from (*1*) the propane–butane mixture diluted with hydrogen ((C_3H_8–C_4H_{10}) : H_2 = 10 : 5 mol/mol) and (*2*) 1,3-butadiene diluted with hydrogen (C_4H_6 : H_2 = 1 : 20 mol/mol).

The second promoter was introduced at the catalyst coprecipitation stage. In addition, it was necessary to see to what extent the replacement of 1,3-butadiene with the commercial propane–butane mixture changes the characteristics of the resulting carbon nanotubes.

The methods of investigation employed in this study were described in a previous publication [13].

RESULTS AND DISCUSSION

Our earlier data [13] facilitate solution of the above problems. The problem of increasing the productivity of the catalyst does not reduce only to enhancing its activity. The productivity of the catalyst in the process considered depends equally strongly on its active service life (i.e., on its stability and operation time before deactivation). Furthermore, in some cases, enhancing the activity of the catalyst leads to a situation such that hydrocarbon decomposition yielding carbon proceeds at a higher rate than the diffusion transport of carbon from the places of its formation (frontal side of the catalyst particle) to the places of its condensation into a phase (rear side of the particle) [4, 5]. In this case, the catalyst loses activity rapidly because of being blocked with carbon.

So, the problem was to strike a favorable balance between the rate of hydrocarbon decomposition and the rate of diffusion of the resulting carbon through the catalyst bulk toward the forming carbon phase.

For this purpose, we sought such an admixture for the earlier developed MoO_3–Fe_2O_3–Al_2O_3 catalyst that could increase the hydrocarbon decomposition rate. From this standpoint, the most promising admix-

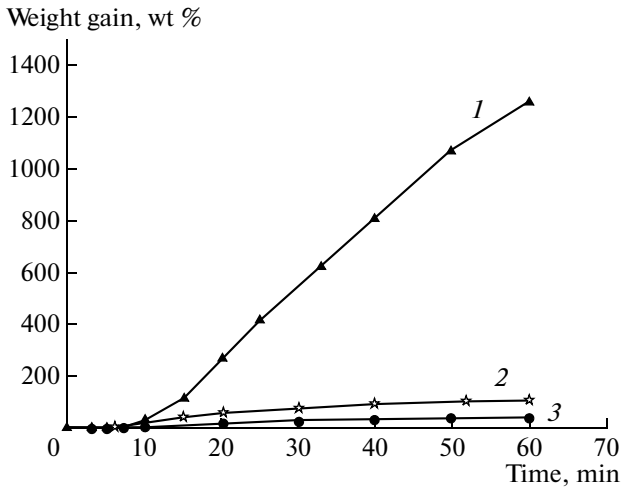

Fig. 2. Kinetics of the formation of carbon nanofilaments from natural gas at 600°C on (*1*) 6.5% MoO_3–40% NiO–Al_2O_3, (*2*) 6.5% MoO_3–40% CoO–Al_2O_3, and (*3*) 6.5% MoO_3–40% Fe_2O_3–Al_2O_3.

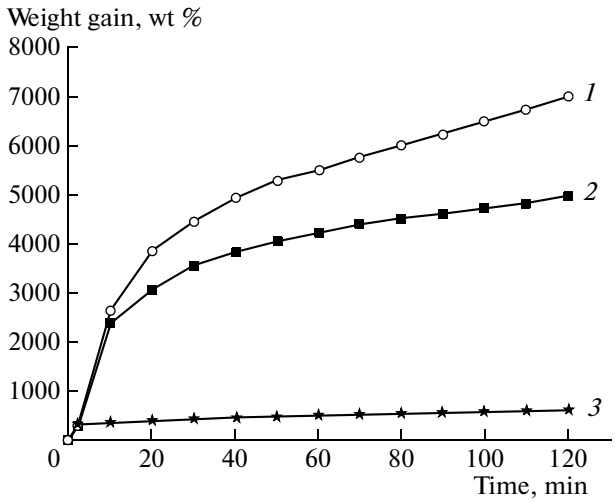

Fig. 3. Kinetics of carbon nanotube formation from 1,3-butadiene diluted with hydrogen (C_4H_6 : H_2 = 1 : 20 mol/mol) at 700°C on (*1*) 6.5% MoO_3–52% Fe_2O_3–Al_2O_3, (*2*) 6.5% MoO_3–52% CoO–Al_2O_3, and (*3*) 6.5% MoO_3–52% NiO–Al_2O_3.

tures are the iron-group metals Co and Ni, which are also active in the synthesis of carbon nanotubes. Since the diffusion coefficient of carbon atoms in iron is two orders of magnitude larger than that of carbon atoms in Co or Ni [14], it was expected that the introduction of small amounts of Co or Ni into the catalyst would raise its hydrocarbon decomposition activity without changing the rate-limiting step of the process or bringing risk of deactivation.

Initially, it was necessary to rank the iron-metals according to their activity in the process examined. To do this, we recorded carbon buildup curves under conditions such that the rate of the overall carbon formation process was limited by hydrocarbon decomposition. It was necessary that the results of these measurements be unaffected by carbon diffusion from the frontal side to the rear side, even though the iron-group metals differed in activity. For these conditions to be satisfied, we chose to use methane (natural gas), the most stable hydrocarbon. Its decomposition via the carbide cycle mechanism at 600°C proceeds so slowly that carbon diffusion from the frontal side of the catalyst particle to its rear side has no significant effect on the measured activity.

Figure 2 illustrates the kinetics of the formation of nanosized carbon products from natural gas containing 97% methane. Clearly, the activity of iron-group metals decreases in the following order: Ni > Co > Fe.

It turned out, however, that this order of activities is valid only when the measured process rate is unaffected by the diffusion transport of carbon and by catalyst deactivation. For iron, the diffusion transport of carbon from the frontal side of the catalyst particle to its rear side at the optimum temperature of 700°C is not the rate-limiting step in any case.

Figure 3 presents the kinetics of carbon nanotube formation from butadiene on MO–MoO_3–Al_2O_3 catalysts in which MO is an iron-group metal oxide. It is clear from Fig. 3 that the iron-based catalyst (6.5% MoO_3–52% Fe_2O_3–Al_2O_3) are more efficient than the catalysts based on cobalt (6.5% MoO_3–52% CoO–Al_2O_3) and nickel (6.5% MoO_3–52% NiO–Al_2O_3). On passing from natural gas (methane) to the commercial propane–butane mixture or 1,3-butadiene, the rate-limiting step of the process on the Fe-containing catalyst does not change. For the Ni- and Co-containing catalysts, diffusion plays the crucial role in carbon nanotube growth, and the more rapid the decomposition of the hydrocarbon, the greater the diffusion effect. Intensive diffusion flows of carbon through the bulk of the catalyst particle bring metal fragments of the catalyst into the carbon phase on the rear side of the particle. In addition, the frontal side of the catalyst particle in this case is partially blocked by carbon. The 6.5% MoO_3–52% NiO–Al_2O_3 catalyst is deactivated at the highest rate, losing its activity within the initial 5 min. As a consequence the above order of activities is not the decisive criterion for selecting a promoter. Owing to the occurrence of deactivation processes, the order of activities appears as Fe > Co > Ni and acquires another meaning. It describes not the catalytic activity, but the productivity of the catalyst in a process occurring at a decreasing rate.

Thus, it was pertinent to test nickel and cobalt oxides as promoters. Preliminary experiments on NiO demonstrated that, due to the high catalytic activity of nickel, the addition of NiO to the MoO_3–Fe_2O_3–Al_2O_3 catalyst causes intensive diffusion transport of carbon through the catalyst bulk, intensive carry-over of catalyst fragments, and their dispersion in the forming carbon phase. As a consequence, we observed

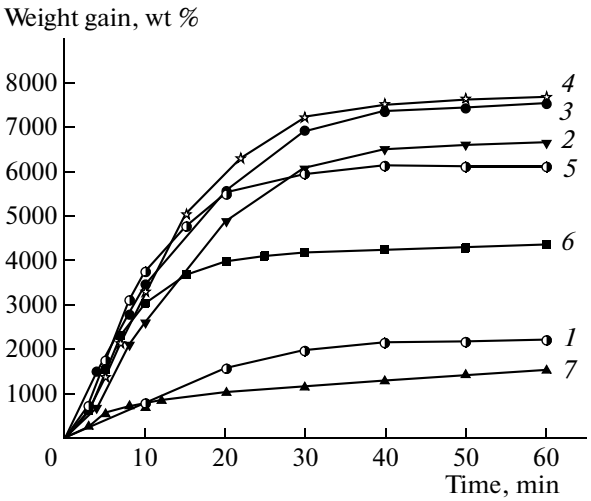

Fig. 4. Kinetics of carbon nanotube formation at 700°C from the propane–butane mixture diluted with hydrogen ($(C_3H_8–C_4H_{10})$: H_2 = 10 : 5 mol/mol) on the 7% MoO_3–52% Fe_2O_3–Al_2O_3 catalyst modified with various amounts of cobalt oxide: (*1*) 7% MoO_3–52% Fe_2O_3–Al_2O_3, (*2*) 10% CoO–7% MoO_3–42% Fe_2O_3–Al_2O_3, (*3*) 21% CoO–7% MoO_3–33% Fe_2O_3–Al_2O_3, (*4*) 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3, (*5*) 40% CoO–7% MoO_3–16% Fe_2O_3–Al_2O_3, (*6*) 46% CoO–7% MoO_3–14% Fe_2O_3–Al_2O_3, and (*7*) 58% CoO–7% MoO_3–Al_2O_3.

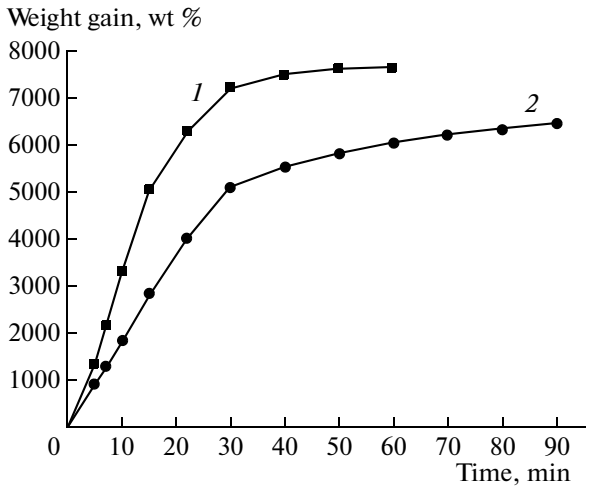

Fig. 5. Kinetics of carbon nanotube formation at 700°C (*1*) on the 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 catalyst from the propane–butane mixture diluted with hydrogen ($(C_3H_8–C_4H_{10})$: H_2 = 10 : 5 mol/mol) and (*2*) on the 7% MoO_3–52% Fe_2O_3–Al_2O_3 catalyst from 1,3-butadiene diluted with hydrogen (C_4H_6 : H_2 = 1 : 20 mol/mol).

more rapid catalyst deactivation and, accordingly, a decline in its productivity—paradoxical result. For this reason, we chose cobalt oxide as the promoter. Our studies of the effect of the cobalt oxide content on the activity of the MoO_3–Fe_2O_3–Al_2O_3 catalysts showed that the most favorable balance between the decomposition rate of the propane–butane mixture and the rate of the diffusion transport of carbon atoms from the frontal part of the promoted catalyst particle is attained with the sample containing 31 wt % CoO (Fig. 4). Then productivity of this promoted catalyst exceeded our expectations. It turned out that its productivity in the decomposition of the propane–butane mixture is even higher than the productivity of the initial catalytic system MoO_3–Fe_2O_3–Al_2O_3 in 1,3-butadiene decomposition (Fig. 5).

The possibility of obtaining carbon nanotubes with the maximum length can be explained in terms of the carbide cycle mechanism as follows. The tube length depends on the diffusion transport rate, i.e., the diffusion coefficient of carbon in metal nanoparticle bulk. Iron is the optimum metal in this respect. The smaller the diameter of the iron particle, the shorter the diffusion path of carbon and the higher the carbon concentration gradient between the frontal and rear sides of the catalyst particle. All these circumstances provide favorable conditions for rapid growth of the carbon phase as long nanotubes.

The rate of the linear growth of carbon nanotubes on the Mo–Fe–Al_2O_3 catalyst from acetylene at 700–750°C was measured to be (1–2) × 10^4 nm/min [15, 16]. Since the intensive carbon growth time for our catalyst 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 at 700°C is 20 min (Fig. 5), the linear rate of nanotube growth on this catalyst is 10^4 nm : 20 min = 500 nm/min, which is one order of magnitude lower.

Therefore, in our case the rate-limiting step of the overall process is the decomposition of the hydrocarbons (propane and butane) on the frontal side of the catalytic nanoparticle.

The high activity of the catalytic nanoparticles and the absence of a significant effect of diffusion enabled us to selectively synthesize long carbon nanotubes with highly uniform characteristics.

Figure 6a presents a typical electron micrograph[1] of carbon nanotubes obtained by the decomposition of the propane–butane mixture on the 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 catalyst at 700°C. Figure 6b shows a fragment of such a nanotube. Electron microscopic examination of the parameters and structure of the resulting nanotubes provided an estimate of their characteristics. The outer diameter of the tubes varies between 10 and 20 nm, with a dominant value of 12–15 nm. The inner diameter of the tubes ranges between 6 and 10 nm. The wall thickness is 2–5 nm and is made up of 6–14 graphene sheets. The filament length is up to 10^4 nm. The selectivity of the process in terms of the proportion of nanotubes with preset characteristics in the total amount of nanotubes is about 95%.

Of special interest is the bend angle of the graphite hexagons in the inner wall of the nanotubes. The circumference of the inner wall of a nanotube 6.5 nm in

[1] The authors are grateful to V.I. Zaikovskii for providing this image.

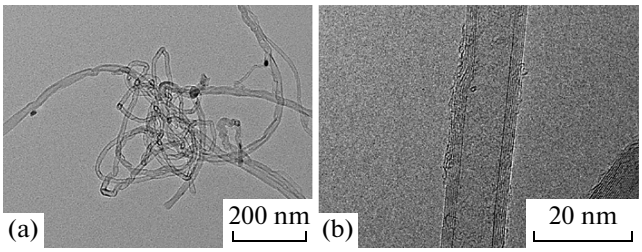

Fig. 6. Electron micrographs of (a) carbon nanotubes obtained by the decomposition of the propane–butane mixture on the 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 catalyst at 700°C and (b) a fragment of such a nanotube.

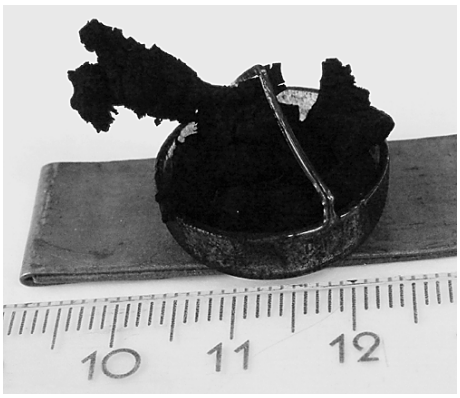

Fig. 7. Carbon phase formed on the 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 catalyst at 700°C. The initial catalyst charge is 2 mg.

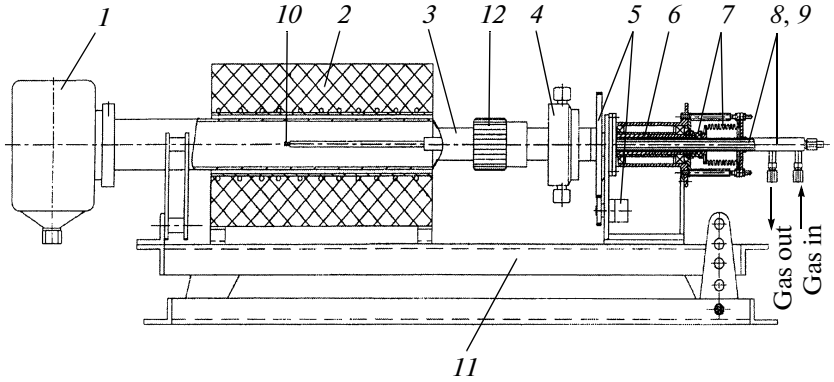

Fig. 8. Continuous rotary reactor: (*1*) discharge bin, (*2*) resistance furnace, (*3*) body of the reactor, (*4*) charging chamber, (*5*) drive, (*6*) hollow shaft, (*7*) bellows, (*8*) gas inlet, (*9*) gas outlet, (*10*) thermocouple well, (*11*) cradle, and (*12*) nut.

diameter is 20.4 nm. The distance between *meta* carbon atoms in the graphite hexagon is 0.249 nm. Hence, the inner circumference of the nanotube accommodates 20.4 nm : 0.249 nm ≈ 82 graphite hexagons, each distorted by 360° : 82 ≈ 4.4°.

Earlier, we designed a horizontal reactor for obtaining nanosized carbon materials [6]. In the design of this reactor, it is taken into account that the volume of the catalyst charge increases by a factor of several tens or even hundreds owing to the resulting carbon phase. By way of example, we present a micrograph of the carbon phase that formed on 2 mg of the 31% CoO–7% MoO_3–24% Fe_2O_3–Al_2O_3 catalyst placed in the reaction basket of a McBain balance (Fig. 7). The volume of the resulting carbon phase is 600 times larger than the volume of the initial catalyst.

The earlier designed reactor was a batch one. It had to be stopped to take out the product and to load a new portion of the catalyst.

Now we have designed a rotary continuous reactor allowing the product to be taken out gradually and the catalyst to be fed continuously. This reactor is schematized in Fig. 8.

CONCLUSIONS

Based on the theoretical understanding of the catalytic decomposition of hydrocarbons and the formation of nanosized carbon materials via the carbide cycle mechanism, we have developed a new, efficient catalyst and technology for the synthesis of carbon nanotubes with a narrow diameter distribution.

The new technology makes it possible to replace butadiene, an expensive precursor, with the commercial propane–butane mixture without impairing the nanotube synthesis efficiency.

The characteristics of the resulting carbon nanotubes have been determined.

A plant comprising a continuous rotary reactor has been designed for obtaining nanosized carbon materials.

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