ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 2, pp. 293–298. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.V. Chesnokov, V.I. Zaikovskii, A.S. Chichkan', R.A. Buyanov, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 2, pp. 310–316.

Growth of Carbon Nanotubes from Butadiene on a Fe–Mo–Al_2O_3 Catalyst

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Received December 23, 2008

Abstract—The MoO_3–Fe_2O_3–Al_2O_3 catalysts were prepared from metal nitrates using a coprecipitation method. It was found that the modification of an alumina–iron catalyst with molybdenum oxide resulted in the formation of a solid solution based on hematite, in which a portion of iron ions was replaced by aluminum and molybdenum ions. The MoO_3–Fe_2O_3–Al_2O_3 catalyst was reduced with a reaction mixture at 700°C. Under the action of 1,3-butadiene diluted with hydrogen, the solid solution based on hematite was initially converted into magnetite and then into an Fe–Mo alloy. The modification of an alumina–iron catalyst with molybdenum oxide considerably changed its properties in the course of carbon nanotube formation. As the Mo content was increased, the yield of carbon nanotubes passed through a maximum. The optimum catalyst was 6.5% MoO_3–55% Fe_2O_3–Al_2O_3. The addition of small amounts of MoO_3 (to 6.5 wt %) to the alumina–iron catalyst increased the dispersity and modified the properties of active metal particles: because of the formation of an Fe–Mo alloy, the rate of growth decreased but the stability of carbon nanotube growth and the yield of the nanotubes increased. A further increase in the molybdenum content decreased the yield because molybdenum is inactive in the test process.

DOI: 10.1134/S0023158410020199

INTRODUCTION

Carbon nanotubes have been intensively studied because of their unique electrical, mechanical, and physical properties [1–3]. It is well known [4, 5] that the formation of carbon nanotubes in the catalytic decomposition of hydrocarbons on iron subgroup metals and their alloys with other metals occurs by a carbide cycle mechanism. Good results were obtained with the use of systems based on iron subgroup metals modified with molybdenum. However, the reason for the promoting effect of molybdenum remains unclear. Shajahan et al. [7] explained the promoting effect of Mo on Co by a change in the dispersity of Co nanoparticles. It was stated that the addition of molybdenum to the Co/MgO system resulted in the formation of small Co clusters upon the decomposition of $CoMoO_4$, and carbon nanotubes grew on these clusters. Deng et al. [8] proposed a two-step mechanism for the formation of carbon nanotubes on bimetallic catalysts. The role of the second metal, in particular, molybdenum, can consist in promoting the formation of an intermediate compound from which carbon nanotubes were subsequently formed. The promoter can be spatially separated from the base metal on which nanotubes are formed. A molybdenum precatalyst, which was placed upstream to the catalyst in the pyrolysis gas line, was used in order to noticeably increase the yield of carbon nanotubes formed from methane [9, 10].

Molybdenum and its oxides can also exhibit catalytic properties in the decomposition reactions of hydrocarbons and CO [11]. Li et al. [12] stated that magnesium molybdates are good catalysts for the growth of carbon nanotubes: they undergo reduction under reaction conditions and nanotubes are formed on molybdenum nanoparticles.

Thus, the current concepts of the role of molybdenum in the formation of carbon nanotubes are contradictory.

The aim of this work was to study the growth of carbon nanotubes from butadiene on the Fe–Mo–Al_2O_3 catalyst. Attention was focused on determining reasons for catalyst deactivation.

EXPERIMENTAL

The catalysts were prepared by the coprecipitation of corresponding metal nitrates. The calculated amounts of $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ salts were dissolved in 200 ml of distilled water, and the solutions were then added to another vessel simultaneously with an ammonia solution to maintain pH 9. The resulting precipitate was kept under the mother liquor at room temperature for 30 min; thereafter, it was washed with a large amount of water to neutral pH. A specified amount of $(NH_4)_2MoO_4$ was dissolved in 20 ml of distilled water in an individual vessel, and this solution was added to the precipitate obtained; the

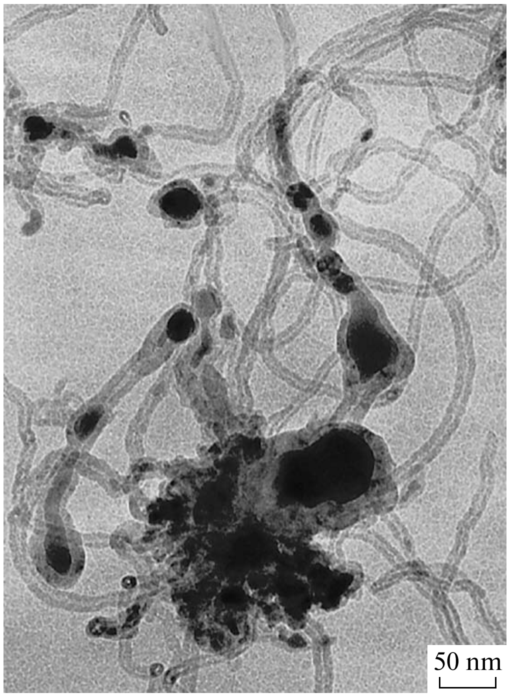

Fig. 1. Morphology of carbon nanotubes formed from 1,3-butadiene diluted with hydrogen on the 55% Fe_2O_3–Al_2O_3 catalyst at 700°C.

contents were stirred, dried, and calcined in a muffle furnace at 350°C for 30 min and then at 500°C for 1 h.

The following catalysts were prepared: 55% Fe_2O_3–Al_2O_3, 3.3% MoO_3–53% Fe_2O_3–Al_2O_3, 6.5% MoO_3–52% Fe_2O_3–Al_2O_3, 7.8% MoO_3–50% Fe_2O_3–Al_2O_3, 14.7% MoO_3–47% Fe_2O_3–Al_2O_3, 20.6% MoO_3–44% Fe_2O_3–Al_2O_3, and 25.7% MoO_3–42% Fe_2O_3–Al_2O_3. As can be seen, the total concentrations of iron and molybdenum oxides varied within the range of 55–67.7 wt %.

The kinetics of formation of carbon nanotubes from 1,3-butadiene was studied in a quartz flow reactor with the McBain balance. The sensitivity of the balance was 1×10^{-4} g. The weight of catalysts was varied from 0.002 to 0.01 g. At the onset of an experiment, the sample was heated in a flow of argon to a specified temperature (usually, 700°C). Butadiene was diluted with hydrogen in order to prevent the occurrence of undesirable side processes of butadiene conversion into tarry matter and to favor the removal of excess carbon from the active surface of metal particles (in some cases, this carbon can block the surface). In preliminary experiments, we found that the dilution of butadiene with hydrogen in the molar ratio $C_4H_6 : H_2 = 1 : 20$ was optimal to reach a high yield of carbon nanotubes.

The purity of 1,3-butadiene was 97.2 vol % (the remainder being butylenes). The purity of argon and hydrogen was 99.99 and 99.9 vol %, respectively.

The X-ray diffraction study of the samples was performed on a D-500 diffractometer (Siemens) using monochromated CuK_α radiation (a graphite monochromator in the reflected beam).

The micrographs of the samples were obtained by high-resolution transmission electron microscopy (HR TEM) on a JEM-2010 electron microscope (JEOL, Japan) with a lattice resolution of 0.14 nm. Energy-dispersive X-ray spectroscopy microanalysis (EDX) was performed on an EDAX spectrometer (EDAX Co) equipped with a Si(Li) detector with an energy resolution of 127 eV.

RESULTS AND DISCUSSION

Initially, we studied the phase composition of the 55% Fe_2O_3–Al_2O_3 catalyst. An analysis of the X-ray diffraction patterns of the sample calcined at 700°C in air demonstrated that the sample contained hematite Fe_2O_3. The unit cell parameters of Fe_2O_3 ($a = 5.013$ Å and $c = 13.691$ Å) were different from tabulated values ($a = 5.0356$ Å and $c = 13.7489$ Å). The ionic radius of Fe^{3+} is 0.079 nm (the coordination number is 6), which is greater than the Al^{3+} ionic radius of 0.067 nm (coordination number, 6). Consequently, a decrease in the unit cell parameters of Fe_2O_3 was due to the replacement of Fe^{3+} ions by Al^{3+} with the formation of a solid solution. Reflections due to other phases were not observed.

The kinetics of growth of carbon nanotubes from 1,3-butadiene diluted with hydrogen in a molar ratio off 1 : 20 at 700°C was studied on the 55% Fe_2O_3–Al_2O_3 catalyst. The catalyst weight increased during the reaction by a factor of about 22 after 2 h. Of course, iron oxide as a catalyst constituent was reduced to the metal under the reaction conditions; therefore, the formula 46% Fe–Al_2O_3 is more correct. The electron-microscopic studies showed that carbon nanotubes formed and grew on the catalyst. Their diameter varied from 5 to 15 nm depending on the size of metal particles, and the length was as large as several micrometers. The growth of nanotubes occurred because of the presence of highly dispersed metal particles at their ends. If iron particles were sufficiently large, the diameter of carbon nanotubes changed in the course of their growth. Initially, it was 30–50 nm; however, it subsequently decreased to 5–15 nm. Note that a portion of the inner cavity of carbon nanotubes was filled with the metal (Fig. 1). It is well known that the diameter of carbon nanotubes depends on the size of metal particles that catalyze the growth. In this case, a decrease in the particle size of Fe caused a change in the tube diameter.

Thus, carbon nanotubes nonuniform in diameter were formed on the alumina–iron catalyst. This result is consistent with previously published data [13].

The modification of the alumina–iron catalyst with molybdenum considerably changed the size and catalytic properties of active metal particles. Table 1 summarizes data on the amount of carbon nanotubes formed from 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 on MoO_3–Fe_2O_3–Al_2O_3 catalysts at 700°C. It can be seen in Table 1 that the yield of carbon nanotubes passed through a maximum as the molybdenum content was increased. The highest yield was obtained at a MoO_3 concentration of 6.5 wt %.

The X-ray diffraction study of the most active 6.5% MoO_3–55% Fe_2O_3–Al_2O_3 catalyst demonstrated that the unit cell parameters after catalyst calcination at 700°C (a = 5.003 Å and c = 13.650 Å) were different from the parameters of Fe_2O_3 (a = 5.013 Å and c = 13.691 Å) in the alumina–iron catalyst. It is likely that, in the hematite phase, a portion of Fe^{3+} ions was replaced by Al^{3+} and Mo^{6+} ions. Molybdenum oxide and alumina phases were absent.

The carbonization of the 6.5% MoO_3–55% Fe_2O_3–Al_2O_3 catalyst at 700°C for 3 min in an atmosphere of 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 resulted only in the partial reduction of Fe_2O_3 and carbon deposition in a 75% amount with respect to the initial sample weight.

As follows from Fig. 2, the major portion of the solid solution of Fe_2O_3 containing aluminum and molybdenum ions was reduced to magnetite (Fe_3O_4). The reflections of magnetite were shifted toward greater angles. The magnetite lattice parameter a decreased to 8.288 Å. Hence, we can conclude that magnetite also contained aluminum and molybdenum ions. According to tabulated data, the Fe_3O_4 lattice parameter is a = 8.396 Å. In addition to magnetite, the X-ray diffraction pattern exhibited the reflections of graphite, iron carbide, and iron metal. The lattice parameter of iron metal somewhat increased to 2.877 Å. In accordance with the Selyakov–Scherrer formula, the solid solution of Mo in Fe contained 4.5% molybdenum. The formation of carbon was due to the presence of an Fe–Mo alloy.

Table 1. Formation of carbon nanotubes from 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 on MoO_3–Fe_2O_3–Al_2O_3 catalysts at 700°C

Catalyst	Increase in the weight of the catalyst as the percentage of its initial weight	
	for 1 h	for 2 h
55% Fe_2O_3–Al_2O_3	1770	2130
3.3% MoO_3–53% Fe_2O_3–Al_2O_3	4300	5130
6.5% MoO_3–52% Fe_2O_3–Al_2O_3	6030	7040
7.8% MoO_3–50% Fe_2O_3–Al_2O_3	5100	5860
14.7% MoO_3–47% Fe_2O_3–Al_2O_3	2970	3500
20.6% MoO_3–44% Fe_2O_3–Al_2O_3	1880	2220
25.7% MoO_3–42% Fe_2O_3–Al_2O_3	1300	1460

The electron-microscopic studies showed that the morphology of carbon deposited on the 6.5% MoO_3–55% Fe_2O_3–Al_2O_3 catalyst under the above conditions corresponds to the formation of carbon nanotubes (Fig. 3). The resulting nanotubes were uniform in diameter. The major portion of the nanotubes had a diameter of 8–12 nm. Using EDX analysis, we found

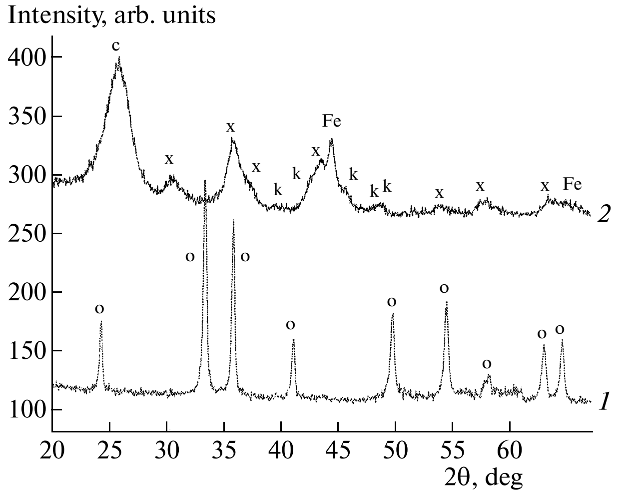

Fig. 2. X-ray diffraction patterns of the 6.5% MoO_3–55% Fe_2O_3–Al_2O_3 catalyst: (*1*) initial sample and (*2*) sample carbonized at 700°C in an atmosphere of 1,3-butadiene diluted with hydrogen for 3 min. Key: o, Fe_2O_3; x, Fe_3O_4; c, C; Fe, Fe; k, Fe_3C.

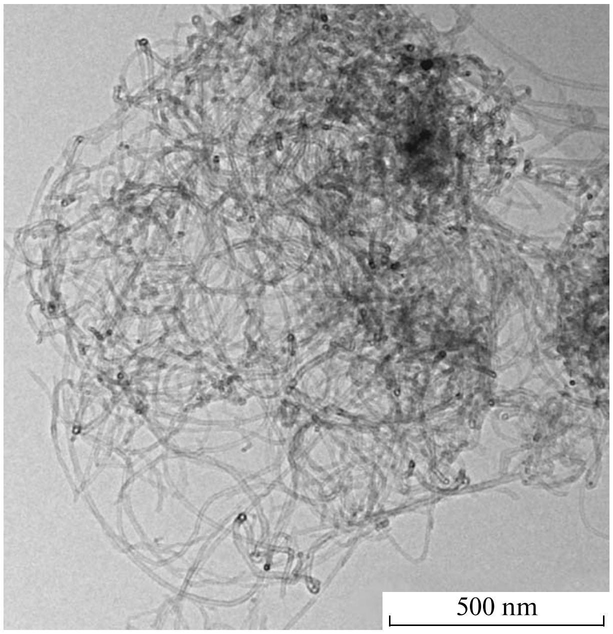

Fig. 3. Electron micrograph of carbon nanotubes formed on the 6.5% MoO_3–55% Fe_2O_3–Al_2O_3 catalyst from 1,3-butadiene diluted with hydrogen at 700°C.

Table 2. Effect of preliminary reduction on the average metal particle size in the carbonized 55% Fe_2O_3–Al_2O_3 and 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalysts

Catalyst	Average metal particle size in the carbonized catalyst*, nm	
	without prereduction	after prereduction for 90 min
55% Fe_2O_3–Al_2O_3	15 nm	110 nm
6.5% MoO_3–52% Fe_2O_3–Al_2O_3	10 nm	30 nm

* The carbon content was 100% with respect to the weight of the initial sample.

that metal particles consisted of iron and molybdenum. On the reduction of iron, molybdenum was also reduced to form an Fe–Mo alloy. This facilitated the stabilization of the size of metal particles to prevent their aggregation. Because of this stabilization, the major portion of iron was retained as particles of size 8–12 nm.

The stabilizing effect of molybdenum was supported experimentally by studying the dispersion of metal particles in the carbonized 55% Fe_2O_3–Al_2O_3 and 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalysts. The carbon content of these catalysts was 100% with respect to the initial sample weight. Table 2 summarizes the X-ray diffraction data on the average particle sizes of iron and the Fe–Mo alloy in the carbonized 55% Fe_2O_3–Al_2O_3 and 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalysts. The addition of molybdenum increased the dispersity of metal particles. The prereduction of both of the catalysts in a flow of hydrogen at 700°C caused the growth of metal particles as a result of agglomeration. The reduction of the 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalyst for 90 min resulted in the agglomeration of its particles, and the particle diameter increased to 30 nm. Because of this, the rate of growth of carbon nanotubes decreased and their yield became lower than that on the unreduced catalyst by a factor of 2.5–3.

Figure 4 shows the initial portions of the kinetic curves of carbon nanotube formation from 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 on the 55% Fe_2O_3–Al_2O_3 and 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalysts at 700°C. It can be seen that the introduction of a molybdenum additive decreased the initial rate of the process. On the 55% Fe_2O_3–Al_2O_3 catalyst, it was higher than that on 6.5% MoO_3–52% Fe_2O_3–Al_2O_3, although the average particle size of Fe (about 15 nm) in the former was greater than the average particle size of the Fe–Mo alloy (about 10 nm).

Thus, the initial dispersity of metal particles is not the only factor responsible for the stable growth of carbon nanotubes. A comparison between the kinetic curves of carbon nanotube formation on the 55% Fe_2O_3–Al_2O_3 (without preliminary reduction) and 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 (after prereduction at 700°C for 90 min) catalysts showed that the alumina–iron catalyst modified with molybdenum was characterized by a higher stability (Fig. 5). However, the initial dispersity of iron particles in the 55% Fe_2O_3–Al_2O_3 catalyst was higher than the dispersity of the Fe–Mo

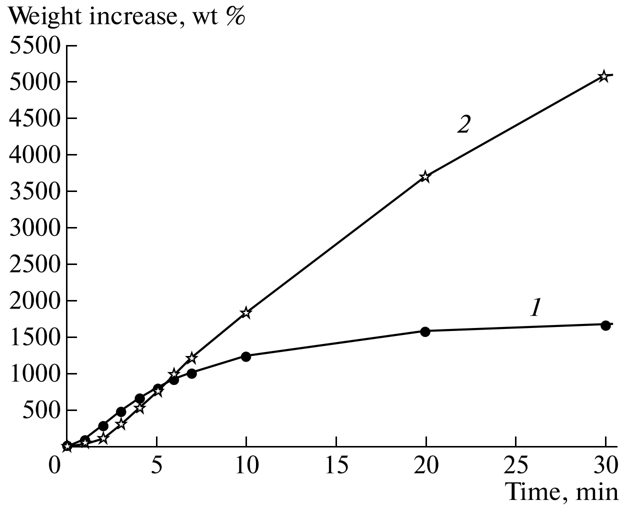

Fig. 4. Initial portions of the kinetic curves of carbon nanotube formation from 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 at 700°C on the following catalysts: (*1*) 55% Fe_2O_3–Al_2O_3 and (*2*) 6.5% MoO_3–52% Fe_2O_3–Al_2O_3.

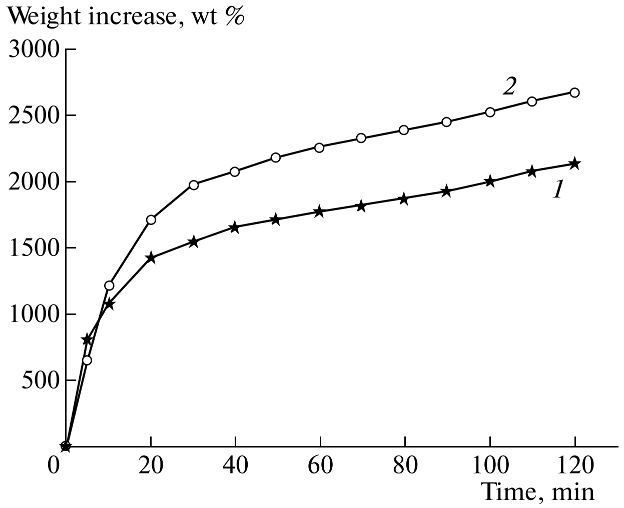

Fig. 5. Kinetic curves of carbon nanotube formation from 1,3-butadiene diluted with hydrogen in a molar ratio of 1 : 20 at 700°C on the following catalysts: (*1*) 55% Fe_2O_3–Al_2O_3 and (*2*) 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 (after reduction at 700°C for 90 min).

alloy in the 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 sample prereduced at 700°C for 90 min (Table 2).

Thus, we can make a conclusion on the role of molybdenum and the mechanism of its stabilizing effect. The prereduction of catalysts that either contained or did not contain molybdenum with hydrogen led to agglomeration. However, even at this step, the catalyst with no molybdenum additive underwent agglomeration several times more rapidly. The special role of Mo manifested itself when the reduction of oxide catalysts occurred immediately in the course of carbonization. In this case, the samples unstabilized with molybdenum have managed to undergo agglomeration and deactivation even at the onset of the process of their reduction and carbon deposition. At the same time, the catalysts containing molybdenum were reduced more slowly and carbonized in the course of reduction. The stabilizing effect of molybdenum manifested itself until the resulting carbon, which prevented the agglomeration of metal particles, began to perform this function. Because of this, metal particles acquired minimum sizes with a very narrow range of varying them.

According to the current concepts of a carbide cycle mechanism, the growth of carbon nanotubes occurred because of the decomposition of a hydrocarbon at the face surface of a metal particle and the diffusion of the resulting carbon atoms through the bulk of the particle. It is well known that the diffusion coefficient of carbon through the bulk of iron metal is higher by two orders of magnitude than that through the bulks of Ni and Co. A too intense diffusion flow of carbon atoms causes the transition of iron particles to exotic states when their inner structure becomes distorted. In this case, vast supersaturation with carbon results in a decrease in the melting temperature of iron particles. As a result, the metal is transferred to a viscous-flow state in which it is easy to undergo fragmentation and propagate in the hollow channel of the carbon nanotube. In some publications [14, 15], it was stated that iron metal particles can occur in a liquid state at 700–900°C in the course of the growth of carbon nanotubes. The propagation of iron metal through the channels of carbon nanotubes dramatically inhibits the growth of the nanotubes. The rate of growth of carbon nanotubes decreases because of the formation of an Fe–Mo alloy. An increase in the molybdenum content will decrease both the rate of the catalytic reaction of butadiene degradation on the surface of the Fe–Mo alloy and the rate of diffusion of carbon atoms through the bulk of the particle.

Thus, the addition of molybdenum to the alumina–iron catalyst increases the dispersity and changes the properties of active metal particles; because of this, the rate of growth of carbon nanotubes decreases, but the growth becomes more stable.

In Table 1, it can be seen that, at molybdenum oxide concentrations in the catalysts higher than 6.5%, the rate and stability of growth of carbon nanotubes decreased. The electron-microscopic studies demonstrated that carbon formed on the 14.7% MoO_3–47% Fe_2O_3–Al_2O_3 catalyst from 1,3-butadiene diluted with hydrogen at 700°C retained the morphology of carbon nanotubes. The diameter of these nanotubes was mainly 6–10 nm, and only a small portion of them had a diameter increased to ~30 nm.

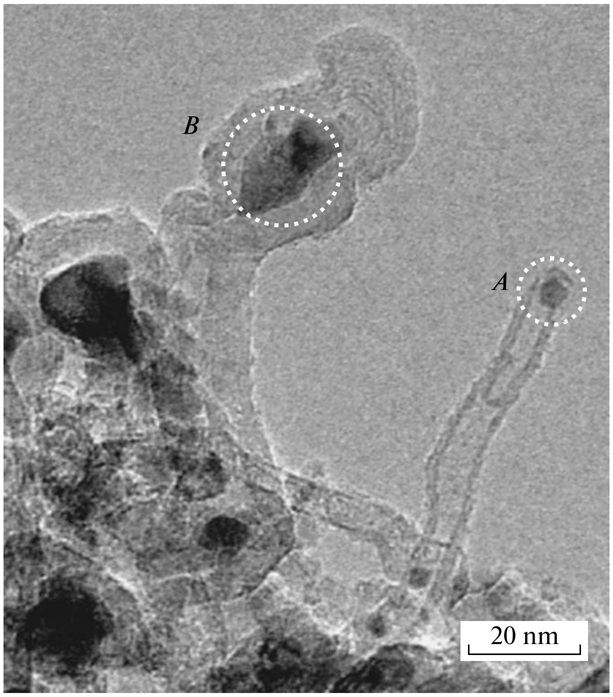

Fig. 6. Electron micrograph of Mo–Fe alloy particles formed on the 14.7% MoO_3–47% Fe_2O_3–Al_2O_3 catalyst from 1,3-butadiene diluted with hydrogen at 700°C. The particles whose composition was analyzed by EDX are marked as *A* and *B*.

Using EDX analysis, we determined the elemental composition of a great number of Mo–Fe alloy particles formed in the carbonized 14.7% MoO_3–47% Fe_2O_3–Al_2O_3 catalyst. We found that the molybdenum content of alloy particles shown in Fig. 6 depended on particle size. Thus, a particle 6 nm in diameter arranged at the end of a tube contained 21.9 at % Mo and 78.1 at % Fe. A particle 37 nm in diameter was coated with graphite layers, and it contained 4.2 at % Mo and 95.8 at % Fe. Consequently, the smaller the particle size, the higher the concentration of molybdenum in the particle.

Thus, an excess concentration of molybdenum decreased the activity of MoO_3–Fe_2O_3–Al_2O_3 catalysts. The Fe–Mo alloy particles of size greater than 15–20 nm exhibited low activity even at a low concentration of molybdenum in them. Only the highly dispersed Fe–Mo alloy particles of size 6–10 nm exhibited high activity. However, they lost their activity with time. In some cases, metal particles were detected in the hollow channels of tubes. These inclusions mainly consisted of iron. An active Fe–Mo alloy particle, which catalyzed the growth of carbon nanotubes, was enriched in molybdenum, whereas iron metal propagated through the channel of the tube. Therefore, the decrease in the activity of the 14.7% MoO_3–47% Fe_2O_3–Al_2O_3 catalyst during the formation of nanotubes is due to the enrichment of the Fe–Mo alloy particles with molybdenum.

In general, the results of this work are reduced to the following conclusions:

(1) Nanosized carbon tubes are formed on the decomposition of hydrocarbons by a carbide cycle mechanism on the $m MoO_3$–$n Fe_2O_3$–$k Al_2O_3$ catalysts synthesized by the coprecipitation method.

(2) In the absence of molybdenum ($m = 0$), the catalyst rapidly loses its activity. A portion of iron is removed to the hollow channel of carbon nanotubes; because of this, the size of metal particles decreases. In addition, iron particles can undergo agglomeration before carbonization. These changes do not allow one to obtain monosized metal particles and carbon nanotubes uniform in diameter.

(3) The introduction of molybdenum into the catalyst prevents the agglomeration of metal particles, retains their high dispersity, and provides a narrow range of scatter of particle sizes. Because of this, carbon nanotubes with a narrow diameter distribution (8–12 nm) can be obtained.

(4) The activity of the catalysts passes through a maximum as the molybdenum content is increased. At a molybdenum concentration lower than the optimum value, the positive effect of molybdenum is lost, whereas the activity of the catalyst decreases at a higher concentration because pure molybdenum is inactive in the test process.

(5) In the course of the formation of carbon nanotubes, the catalytically active Fe–Mo alloy particles are enriched in molybdenum because of the removal of iron particles into the cavities of nanotubes.

(6) The use of the 6.5% MoO_3–52% Fe_2O_3–Al_2O_3 catalyst allows us to obtain carbon nanotubes in high yields from butadiene with a narrow diameter distribution.

ACKNOWLEDGMENTS

This work was performed in the framework of a joint program of basic research of the Siberian Branch and OKhNM of the Russian Academy of Sciences (project no. 139-522); it was supported by Russian Foundation for Basic Research (project no. 07-08-00339).

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