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Synthesis of Carbon Nanomaterials from Hydrocarbon Feedstock Using Ni/SBA-15 Catalyst

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Abstract

A synthesis of carbon nanomaterials was performed *via* decomposing hydrocarbon feedstock having various compositions (natural gas, propane–butane mixture) at 700 °C using a 20 % Ni/SBA-15 nickel catalyst. As the carrier for nickel catalysts we used mesoporous silicate material SBA-15 with a fixed pore diameter. It has been demonstrated that the preliminary functionalization of the carrier with amino groups provides a high dispersity of nickel particles due to their stabilization within the channels of the mesoporous silicate matrix. The maximal yield of carbon nanomaterials (27 g/g_{Ni}) was achieved in case of using a mixture of C_3-C_4 . The product is presented by hollow carbon nanofibers with a diameter of 10–50 nm. The HRTEM method demonstrated that the formation of carbon filaments occurred owing to active centers attached to the outer surface of the carrier. The metal particles located within the pores of the SBA-15 matrix do not participate in the process. An effect of carbon methanation exerted on the yield of a carbon nanomaterial and its morphological features has been studied.

Key words: mesoporous silicates, SBA-15, carbon nanofibers, catalytic decomposition, hydrocarbon feedstock, natural gas, propane, butane, carbide cycle

INTRODUCTION

Unique physicochemical properties of carbon nanomaterials (CNM), including carbon nanofibers, nanotubes, fullerenes, are responsible for the attractivity thereof both from the standpoint of applications, and from the fundamental point of view. They are widely used in adsorption and catalysis, for water and air purification, energy storage, in developing composite materials, as well as for the purposes of making electrochemical sensors [1].

Today, carbon nanotubes (CNT) and carbon nanofibers (CNF) are usually prepared by means of the catalytic decomposition of hydrocarbons on dispersed metal particles [2]. The main parameters determining the structure of the resulting nanomaterial, as well as composition and size of the active center of a catalyst are presented by the synthesis temperature and type of hydrocarbon raw material [3]. In order to obtain tubes and fibers with a narrow diameter distribution is necessary to use a catalyst with particles of a very close size.

Using any conventional methods of catalyst preparation (the co-precipitation or impregnation of conventional carriers) cannot provide obtaining catalytic particles of the same diameter. It is also known that in the course of heating and reducing the active component there an agglomeration of particles could occur their partial sintering. In order to obtain particles of the catalyst, normalized by size, one uses, for example, structured carriers [4]. For the synthesis of particles within the diameter range of 1-25 nm, mesoporous silicates (KSW-1, FSM-16, MC-41 and SBA-15) that have onedimensional hexagonal channels with a diameter of 2-50 nm are best suited [5].

For example, the authors of [5-7] in order to synthesize carbon nanotubes of the same diameter, incorporated iron particles into the pores of SBA-15 carrier. By varying the pore size of the silicate, the authors obtained a series of multi-walled carbon nanotubes having the diameter required. The authors of [8] for the synthesis of multi-walled carbon nanotubes dispersed FeCo alloy particles within a highly ordered mesoporous silicate SBA-16 (body-centred cubic structure, sp. gr. Im3m). The authors of [9] demonstrated that the introduction of nickel into the pores of SBA-15 increases significantly the stability of the catalyst at high temperatures.

Catalysts containing nickel in a mesoporous matrix are often synthesized by means of incipient wetness impregnation using the solutions of simple precursor nickel salts (nitrates, oxalates *etc.*) [10]. Sometimes one uses the technique of deposition into the pores, as well as impregnating in the excess of the solution with a subsequent slow evaporation, which results in producing 25 nm sized nickel particles [11]. Other methods of applying nickel onto mesoporous silicates include NiCl₂ ion exchange from solutions of Ni(NH₃)₄(NO₃)₂ and a direct incorporation of Ni²⁺ ions in the course of synthesizing the carrier *via* a sol–gel method.

The authors of a number of papers use a grafting method for the introduction of ions of various metals into the pores of SBA-15 [12–14]. For this purpose, the surface of the silicate is preliminary functionalize by amino groups. This approach was successfully used for the introduction of cobalt [14], nickel [12–14], copper [13, 14], zinc and chromium [13] ions. For the surface modification, one often uses so-called post-synthesis technique [12–15], how-ever, in some investigations; the modified SBA-15 is prepared by means of the co-condensa-

tion of tetraethyl orthosilicate and 3-aminopropyl triethoxysilane (for example, [16]).

In the present study, we attempted obtaining a nickel catalyst with a narrow particle size distribution for subsequent using in the synthesis of CNM from hydrocarbon feedstock. As a mesoporous matrix for the catalyst, we chose silicate SBA-15. For the preparation of a modified carrier, we used 3-aminopropyl trimethoxysilane. The hydrocarbon feedstock was presented by the natural gas (~92 % of CH₄) and communal gas (a mixture of propane and butane).

EXPERIMENTAL

Preparation and modification of SBA-15

In order to obtain mesoporous carrier SBA-15 we mixed 1 M sodium silicate solution with 1.1 M HCl, added a structure-forming agent (surfactant) Pluronic P123 (($EG_{20}PG_{70}EG_{20}$, wherein EG is ethylene glycol, PG is propylene glycol). The surfactant/Si molar ratio was equal to 1 : 100. The solutions were mixed at a room temperature. The resulting white precipitate was withstood for 1 day, then filtered off, dried and calcined at 550 °C.

The modification of SBA-15 was carried out in a reactor with a reflux condenser. The SBA-15 powder was added to a solution of 3-aminopropyl trimethoxysilane in o-xylene. The mixture was brought to boiling under argon to be held for 24 h. The precipitate obtained was filtered off and dried at 110 $^{\circ}$ C.

Synthesis of Ni/SBA-15catalyst

The nickel was deposited into the pores of the modified and original silicate SBA-15 by means of the impregnation technique according to incipient wetness. To prepare the impregnating solution we dissolved a required amount of nickel nitrate in acetone. The catalyst was dried at a room temperature (24 h) and at 90 °C (1 h) and then calcined at 500 °C. for 2 h. Following this procedure we obtained samples of catalyst containing 20 mass % of Ni (as calculated with respect to metallic nickel).

Catalytic pyrolysis of hydrocarbon feedstock

The synthesis of carbon nanofibers was carried out in a flow reactor equipped with a McBen balance, which allowed tracking the change in the mass of a sample during the experiment. A weighed sample portion of catalyst (4.00 ± 0.05) mg was loaded into the reactor that was purged with argon to remove oxygen and then heated up to 700 °C. The sample was then reduced in a hydrogen flow for 15 min, further the reactor was fed with natural gas or propane-butane mixture.

Studying the samples of catalysts and carbon nanomaterials

The temperature programmed reduction (TPR) of the catalyst samples was carried out in a flow-through reactor with a McBen balance. The reactor with a sample loaded (40.0 ± 0.1 mg) was purged with argon, and then hydrogen was fed at a rate of 10 L/h. The reactor temperature was increased at the rate of 5 °C/min.

The morphology of the catalysts samples and carbon product was examined by means of the high resolution transmission electron microscopy (HRTEM). The micrographs were recorded on a JEM-2010CX transmission electron microscope (the accelerating voltage is 100 kV, the spherical aberration coefficient of the objective lens is 2.8 mm) with the resolution of 1.4 Å with respect to lines.

RESULTS AND DISCUSSION

Investigation of original catalysts

It is known that the surface properties of the carrier determine the distribution character of the salt-precursor of the active component in the course of applying and hence the size of the metal particles under formation. In this regard, it is interesting to investigate carriers with highly ordered pores and functional groups attached to the surface. Let us consider the nature of the reduction of nickel oxide supported on a conventional and amino group-modified silicate SBA-15. Figure 1 demonstrates the TPR profiles of catalysts NiO/SBA-15 and NiO/ SBA-15m. The main part of the initial oxide in the both cases is reduced at the temperature lower than 450 °C; however, the TPR profiles for these samples are significantly different.

The differential curves could be divided into three main areas of reduction, viz., of 210, 310 and 390 °C. The first peak could be associated with the reduction of nickel oxide (III) [17]. As one could see, the surface modification of the carrier SBA-15 leads to increasing this peak intensity with shifting it towards lower temperature values (200 °C). The second peak at 310 °C refers to the reduction of nickel (II) oxide particles, weakly bound with the surface of the carrier [18]. For the modified sample, this peak decreases and also shifts toward lower temperature values. The peak at 390 °C re-



Fig. 1. TPR profiles for samples of catalysts: 1-NiO/SBA-15, 2 - NiO/SBA-15m.

fers to the reduction of particles of nickel that interacts strongly with the carrier, or to the reduction of nickel silicate [17, 18]. This peak disappears almost completely in the course of the carrier modification. The acceleration of the reduction process and observed shifting of the peaks towards lower temperature values could be caused by a smaller particle size of nickel oxide. Thus, the use of the modified carrier allows synthesizing and stabilizing particles of the active component in the highly dispersed state.

In order to confirm this assumption, the catalyst samples obtained after the reduction in hydrogen, were studied by means of the TEM method. Figure 2 demonstrates the histograms of the particles size distribution, plotted according to measuring of more than 300 particles.

It is seen that the modification of the carrier surface leads to the formation of smaller particles. The average particle diameter amounts to 21.8 and 11.4 nm in case of using the original and modified carriers, respectively. It should



Fig. 2. Nickel particle size distribution in the catalysts Ni/SBA-15 (a) and Ni/SBA-15m (b).



Fig. 3. TEM images of the catalyst Ni/SBA-15, reduced in a flow of hydrogen at 700 °C: a – the appearance of the catalyst; b – a high-resolution TEM image.

also be noted that in case of the application of nickel onto the original carrier the metal particles are located mainly on the outer surface and are almost not introduced into the pores (Fig. 3, *a*). The nickel particles could also be located within the mouths of the channels (see Fig. 3, *b*).

In the case of the modified carrier the nickel nanoparticles are predominantly located within the porous structure of the silicate matrix (Fig. 4). It should also be noted that particles located on the outer surface of the carrier are more uniform and less agglomerated, as compared with the unmodified carrier.

Thus, the modification of the SBA-15 carrier surface by amino groups not only leads to an increase in the dispersity level of the active component, but also allows applying nickel particles inside the pores of the carrier, *i. e.* distributing it more uniformly over the volume of the carrier.



Fig. 4. TEM images of Ni/SBA-15m catalyst, reduced in a flow of hydrogen at 700 $^\circ\text{C}.$

Synthesis and investigation of a carbon product

As already mentioned, in the course of CNM synthesis one of the most important factors determining the morphology is presented by the particle size of the active component. This factor also significantly affects the kinetics of the catalytic decomposition of hydrocarbon raw material. Figure 5 demonstrates the kinetic curves for the accumulation of the carbon product on nickel catalysts Ni/SBA-15 and Ni/SBA-15m in the course of the decomposition of natural gas at 700 °C.

It should be noted that in both cases the main mass of the product is already accumulated within the first minute. The high rate of increasing the mass of the carbon product is replaced by a sharp exit of the kinetic curve to the plateau, which indicates the deactivation of the catalyst. In this case, the loss of the catalytic activity is explained by blocking ac-



Fig. 5. Yield of the carbon product in case of natural gas decomposition (700 $^{\circ}\rm{C}$) on catalysts Ni/SBA-15 (1) and Ni/SBA-15m (2).

tive metal particles by the repelling carbon. It follows from the data of Fig. 5 that the previous modification of the carrier provides a uniform distribution over the volume of highly dispersive nickel particles, whereby the carbon



Fig. 6. TEM images of carbon nanofibers synthesized from natural gas at 700 $^{\circ}$ C on catalysts Ni/SBA-15m (*a*) and Ni/SBA-15 (*b*).

product yield exhibits an almost four-fold increase, as compared with the unmodified carrier. The yield of the carbon material on the modified catalyst Ni/SBA-15m amounted to $18.5 g_C/g_{Ni}$.

High-resolution TEM images are demonstrated in Fig. 6. It is seen that the decomposition of hydrocarbons on catalysts Ni/SBA-15 and Ni/ SBA-15m results in the fact that there mainly occurs the formation of carbon nanofibers, whose morphology could be attributed to the so-called pseudo- nanotubes, i. e. nanofibres with a coaxially conical packing of graphene layers, and with a hollow channel inside (see Fig. 6, b). The catalyst particle has a well-determined cutting, which indicates the differentiated role of different faces of the catalyst particles in the course of decomposing the hydrocarbon and the growth of carbon nanostructures. The tail region of the nickel particles is significantly elongated, because it is in a special "liquid-like" state in the course of CNM growth [19]. Upon closer examination one could observe jumpers formed by the basal planes of graphite in the hollow channel of the carbon nanofibers those divide the interior within the fibre body in into separate sectors. The diameter of nanofibres ranges from 10 to 50 nm.

The micrograph (Fig. 7) demonstrates some nickel particles located within the mesoporous matrix of SBA-15m. Consequently, they do not participate in the process of the decomposi-



Fig. 7. TEM image of inactive nickel particles fixed within mesopores of SBA-15m carrier.



Fig. 8. TEM image of nickel particles in the catalyst Ni/SBA-15m, blocked by graphite-like deposits.

tion of hydrocarbons and synthesis of CNM. One of possible reasons of their "inertness" thereof could be a diffusion deceleration that prevents the process of the carbon phase nucleation on the particles encapsulated in the structure of the silicate. Similar observations were described by other researchers [7].

As already noted, the nickel particles have a high activity, but they produce the prevailing part of the product only within the first minutes of the reaction. The catalyst deactivation further observed occurs primarily as a result of blocking the active surface of the nickel particles with carbon. Figure 8 demonstrates a typical micrograph of such a particle.

Influence of the nature of hydrocarbon raw material

The nature of the degradable hydrocarbon raw material also affects considerably the yield of carbon nanomaterials. Kinetic dependences of the yield of CNM on the catalyst 20 % Ni/ SBA-15m, at the decomposition of the natural gas and propane-butane mixture are mapped on Fig. 9. The maximal yield of the carbon product is determined by the rate of catalyst deactivation caused by blocking the active particles by deposition products (see Fig. 8). In case of the decomposition of methane the only one reaction is implemented, moreover, the theoretically possible conversion level of CH_4 is limited by its reversibility:



Fig. 9. Yield of the carbon product at 700 $^{\circ}$ C on the catalyst Ni/SBA-15m in the course of the decomposition of natural gas (1) and propane-butane mixture (2).



Fig. 10. TEM images of carbon nanostructures synthesized on the catalyst Ni/SBA-15m from the propane-butane mixture at 700 °C.

The process of the decomposition of propane and butane molecules at these temperature values is almost irreversible:

$$C_3H_8 \to 3C + 4H_2 \tag{2}$$

$$C_4 H_{10} \rightarrow 4C + 5H_2 \tag{3}$$

However, in parallel with reactions (2) and (3), the process of carbon methanation implemented that is essentially opposite to the reaction (1):

$$C + 2H_2 = CH_4 \tag{4}$$

A partial hydrogenation of the carbon according to reaction (4) leads to the decrease the selectivity level of the process with respect to CNM, but it allows extending the period of the efficient operation of the catalytic particles, thereby the yield of the product increases. On the other hand, owing to the methanation the packing of carbon filaments becomes loosened, whereas carbon has the porous morphology [20].

The studies of the morphology of carbon deposits obtained from a mixture of C_3-C_4 , demonstrated that, as in case of natural gas, the product consists of nanofibers with the diameter of 10–50 nm with a coaxial-conical arrangement of graphene layers. Some fibres have a continuous full channel, however, in most cases this cavity is segmented (Fig. 10).

CONCLUSION

Upon the preparation of carbon nanofibers by the mechanism of the carbide cycle the diameter is mainly determined by the size of a catalytic particle. In this regard, the main task of the preparation of catalysts consists in the synthesis of uniformly sized particles of the active component on the carrier surface. In this case the catalytic system should retain the initial dispersity level of the active component in the hydrocarbon environment at high temperature values (700 °C or higher). In this work, in order to stabilize particles of the active component in we chose a highly ordered mesoporous material based on silicon oxide, viz., SBA-15. The application of nickel nanoparticles inside of the carrier channels has been achieved only in case of the preliminary functionalization of the surface of the silicate matrix by amino groups. However, the further synthesis of carbon nanofibres demonstrated that parti-

cles stabilized in channels of SBA-15 do not participate in the formation of the carbon product. The growth of carbon structures occurred only in contact between hydrocarbons and nickel particles localized on the outer surface of the carrier. In this case, the diameter of the nanofibres produced (10-50 nm) was greater than the diameter of the channels of the carrier (8 nm). To all appearance, the elongated pores of SBA-15 are responsible for a low rate of supplying the hydrocarbon to the metal particles inside the pores, as well as a low rate and low removal rate of hydrogen, whose local excess does not allow the carbon to be formed. Taken together, these factors do not promote the initiation of the carbide cycle mechanism [19]. The HR TEM studies demonstrated that resultant carbon product is characterized by a high morphological homogeneity and consists of thin coaxial conical nanofibers with a hollow channel.

REFERENCES

- 1 Thostenson E. T., Ren Z., Chou T.-W., Comp. Sri. Technol., 61, 13 (2001) 1899.
- 2 Buyanov R. A., Chesnokov V. V., Katal. Prom-sti, 2, (2006) 3.
- 3 Lee C. J., Lyu S. C., Cho Y. R., Lee J. H., Cho K. L., Chem. Phys. Lett., 341, 3-4 (2001) 245.

- 4 Kobayashi K., Kitaura R., Nishimura F., Yoshikawa H., Awaga K., Shinohara H., Carbon., 49 (2011) 5173.
- 5 Lo A.-Y ., Yu N., Huang S.-J., Hung C.-T., Liu S.-H., Lea Z., Kuo C.-T., Liu S.-B., *Diamond & Rdated Mater.*, 20 (2011) 343.
- 6 Lo A.-Y., Liu S.-H., Huang S.-J., Shen H.-K., Kuo C.-T., Liu S.-B., Stud. Surf. Sci. Catal., 165 (2007) 409.
- 7 Wang X. Q., Wang M., Jin H. X., Li Z. H., He P. M., Appl. Surf. Sci., 243, 1–4 (2005) 151.
- 8 Carta D., Casula M. F., Corrias A., Falqui A., Dombovari A., Galos A., Konya Z., J. Nanosci. Nanotechnol., 11, 8 (2011) 6735.
- 9 Zhang M. Ji S, Hu L., Yin F., Li C., Liu H., Chin. J. Catal., 27, 9 (2006) 777.
- 10 Park Y., Kang T., Lee J., Kim P., Kim H., Yi J., Catal. Today, 97 (2004) 195.
- 11 Gomez-Reynoso R., Ramirez J., Nares R., Luna R., Murrieta F., Catal. Today, 107, 108 (2005) 926.
- 12 Zhao S., Zhao J., Lou L.-L. Liu S., Micropor. Mesopor. Mater., 137 (2011) 36.
- 13 Hernandez-Morales V., Nava R., Acosta-Silva Y. J., Macias-Sanchez S. A., Perez-Bueno J. J., Pawelec B., *Micropor. Mesopor. Mater.*, 160 (2012) 133.
- 14 Rivera-Jimenez S. M., Mendez-Gonzalez S., Hernandez-Maldonado A., Micropor. Mesopor. Mater., 132 (2010) 470.
- 15 Nguyen T. P. B., Lee J.-W., Shim W. G., Moon H., Micropor. Mesopor. Mater., 110 (2008) 560.
- 16 Wang X., Lin K. S. K., Chan J. C. C., Cheng S., Chem. Commun., 23 (2004) 2762.
- 17 Mile B., Stirling D., Zammitt M. A., Lovell A., Webb M., J. Catal., 114, 2 (1988) 217.
- 18 Zielicski J., Catal. Lett., 31, 1 (1995) 47.
- 19 Buyanov R. A., Chesnokov V. V., Zh. Prik. Khim., 70, 6 (1997) 978.
- 20 Mishakov I. V., Strel'tsov I. A., Bauman Yu. I., Vedyagin A. A., Buyanov R. A., *Izv. Vuzov. Khim. Khim. Tekhnol.*, 54, 7 (2011) 107.