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Catalysts Based on Filamentous Carbon in the Hydrogenation of Aromatic Compounds

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Abstract—In order to extend the area of application of the base catalytic system metal–filamentous carbon, the catalytic properties of Ni–filamentous carbon catalysts have been tested in the hydrogenation of aromatic compounds (benzene, benzyl cyanide, benzophenone, and nitrobenzene). The selectivity of the catalysts depends on the outer faceting of the active metal particles. The benzene ring is hydrogenated on the (111) face of the metal nanoparticles, whereas the selective hydrogenation of functional groups in substituted aromatic compounds occurs on the surface of active component nanoparticles in which the (111) face is blocked.

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Over several decades, researchers have been expressing persistent interest in carbon nanofilaments resulting from the catalytic decomposition of various hydrocarbons on iron subgroup metals or on their alloys. Such systems are usually studied and used in catalysis as sorbents and supports. We were the first to study metal particles fixed on the ends of carbon filaments (figure), for we concluded that they can serve as active components of catalysts for some reactions. As a result, radically new metal–filamentous carbon catalytic systems were discovered. These systems are active in the reactions that are usually accelerated by metallic catalysts. The properties of Ni–filamentous carbon catalysts were studied most thoroughly in the selective hydrogenation of dienic and acetylenic hydrocarbons into olefins [1–7]. The selectivity of these catalysts depends on what the outer faces of the metal particles are. The outer face type can be controlled by varying the catalytic hydrocarbon decomposition conditions and the nature of the carbon source. Examination of samples with differently faceted particles of the active metal made it possible to evaluate the properties of particular crystallographic faces. For example, it was shown that the hydrogenation of dienic and acetylenic hydrocarbons into olefins occurs on the nickel (110) faces and that these hydrocarbons are totally hydrogenated to alkanes on the (111) and (100) faces.

The purpose of this work was to provide a deeper insight into the new base metal–carbon catalytic system. With the aim of extending the area of application of such systems, we studied the possibility of their use in the selective hydrogenation of substituents at the benzene ring. The study of the catalytic properties of the Ni/C catalysts in the reductive dechlorination of chlorobenzene [2] showed that this area is promising. We observed an interesting feature of these catalysts that could not be explained on the basis of available published data: the benzene ring was hydrogenated on none of the catalysts, while it was known that the nickel catalysts, including those on carbon supports, are fairly active in these reactions. We also demonstrated that the catalytic systems examined here are rather efficient in the hydrogenation of various functional groups in substituted aromatic compounds [5] (Table 1).

The selective hydrogenations of substituents at the benzene ring is of great practical significance because their products are widely used in the chemical industry for the synthesis of various organic compounds, including dyes, drugs, fertilizers, pesticides, and many other substances. In this work, we present the results of our study of the prospects of use of the Ni–filament carbon catalysts in industrially important reactions, namely, the selective hydrogenation of benzyl cyanide, benzophenone, and nitrobenzene. The selective hydrogenation of benzyl cyanide yields important intermediate products of fine organic synthesis and of the synthesis of physiologically active substances (phenylethylamines). Benzhydrol and diphenylmethane, which are used in pharmaceutics, are obtained from benzophenone. The selective hydrogenation of nitrobenzene to aniline is an intermediate step in the production of more complex intermediates, dyes, chemical additives for polymers, pharmaceuticals, pesticides, etc. The selective hydrogenation of substituents at the benzene ring is carried out most frequently on catalysts containing nickel, platinum, or palladium [8–11]. As a rule, the hydrogenation of functional groups is accompanied by the hydrogenation of the benzene ring, which results in the loss of valuable starting compounds and in difficulties in isolating the target products. The eplacement of the platinum and palladium catalysts with the Ni–filamentous carbon

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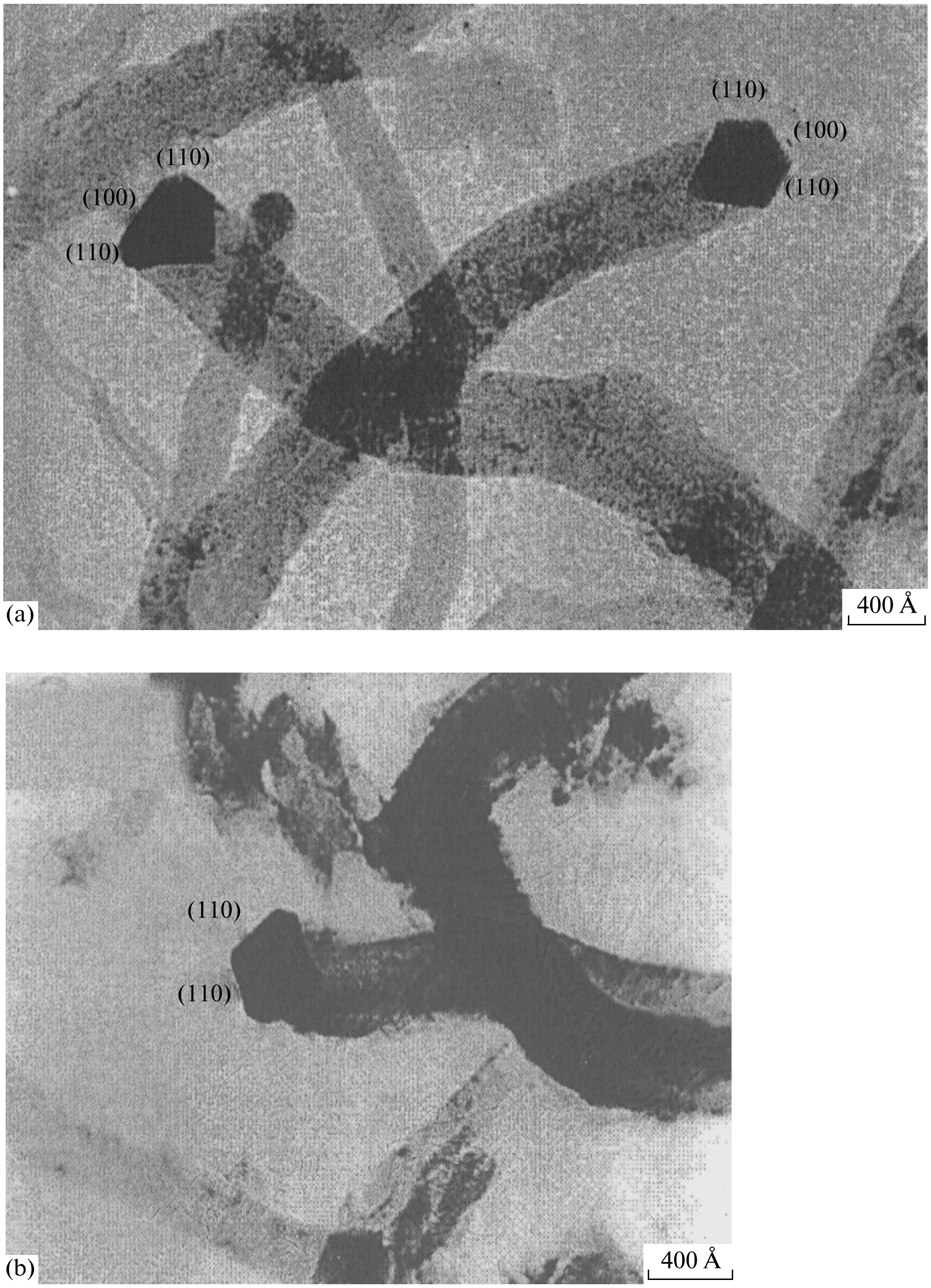


Micrographs of the Ni–carbon catalysts with C/Ni = (a) 1.5 and (b) 10.

system reduces the cost of the process and enhances its selectivity. In addition, the method proposed for the synthesis of metal–carbon catalysts is environmentally friendly, since its use is not accompanied by the formation of wastewater or harmful gas emissions.

We assumed that the crystallographic features of active metal nanoparticles located at the ends of carbon filaments can exert a substantial effect on the selectivity of hydrogenation of aromatic compounds. We believe that the catalysts in which the surface of

Table 1. Hydrogenation of functional groups in the substituted aromatic compounds on the 6.4% Ni/C catalyst based on filamentous carbon [5]

Starting compound	Target product	Product yield, mol %
para-Benzoquinone	Hydroquinone	90
Nitrobenzene	Aniline	100
Benzamide	Benzylamine	74

active metal nanoparticles has no (111) faces are the most promising for the selective hydrogenation of substituents at the benzene ring.

EXPERIMENTAL

Catalysts were synthesized in the Laboratory of Dehydrogenation of the Boreskov Institute of Catalysis (Siberian Branch, Russian Academy of Sciences) by the catalytic decomposition of hydrocarbons according to a standard procedure [1, 5, 6].

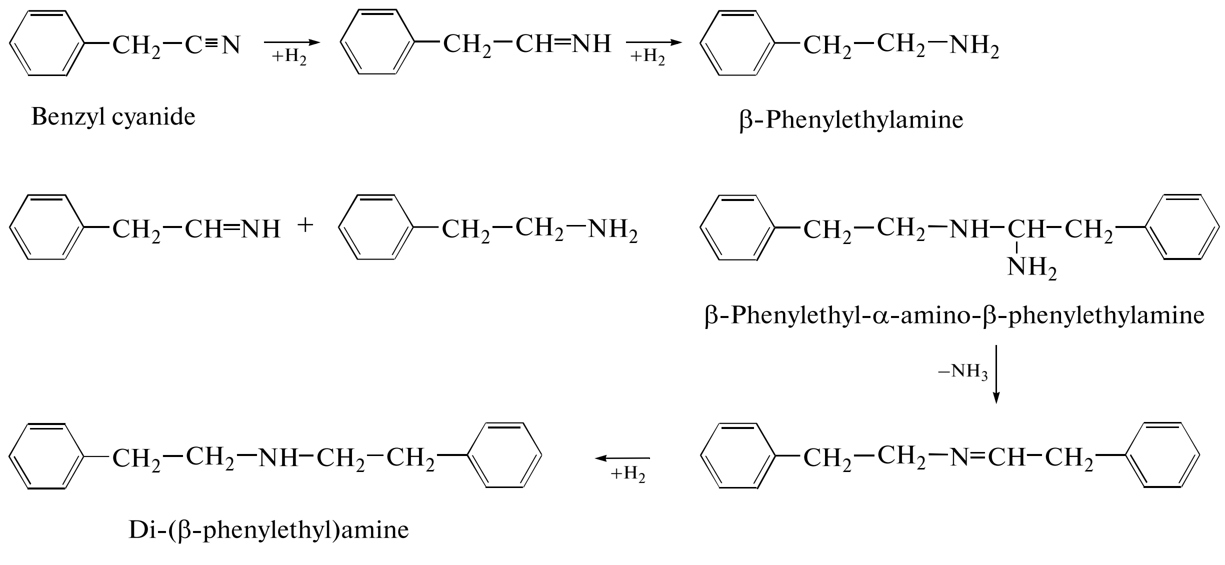
Benzene was hydrogenated in a flow reactor. The testing conditions were as follows: the flow rate of benzene at room temperature was 2 g/h, the flow rate of the benzene–hydrogen vapor mixture fed into the reactor was 6 l/h, the reaction temperature was 100 or 200°C, and the composition of the catalyst was 41.3% Ni/C. The reaction products were analyzed chromatographically using alumina as the adsorbent.

The catalytic properties of the Ni/C samples containing 7 to 30% Ni were tested in benzyl cyanide, benzophenone, and nitrobenzene hydrogenation in a static reactor at an elevated hydrogen pressure. In all cases, 0.8 g of the catalyst was placed in an autoclave equipped with a magnetic stirrer. The hydrogenation of a 10% solution of benzyl cyanide, a 2% solution of benzophenone, and a 10% solution of nitrobenzene in isopropyl alcohol was carried out at pressures of 50, 70, and 50 atm and temperatures of 100, 100, and 120°C, respectively. The hydrogenation time was 4.5, 6, and 5 h, respectively. The reaction products were analyzed by gas chromatography coupled with mass spectrometry (GC-MS) on a Saturn-200 system.

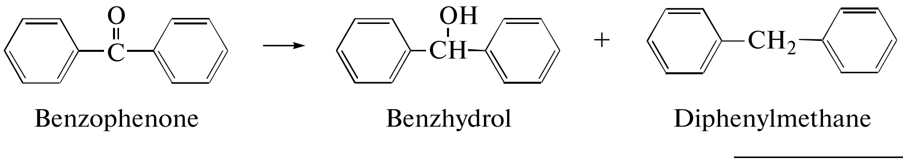
RESULTS AND DISCUSSION

According to the data obtained, cyclohexane is the single product of benzene hydrogenation. The results of testing of the nickel–filamentous carbon catalyst in this reaction are given in Table 2.

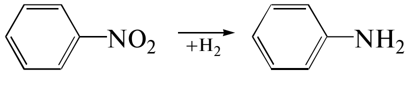
According to GC-MS data, the products of benzyl cyanide hydrogenation on the 30% Ni/C catalyst at 20% substrate conversion contain the starting compounds and secondary amines: di-(β-phenylethyl)amine and β-phenylethyl-α-amino-β-phenylethylamine in a 9 : 1 ratio. To obtain primary amines by nitrile hydrogenation, the reaction should be carried out at a low pressure in an acidic solvent [12, 13]. No products of benzene ring hydrogenation were observed under our experimental conditions.



Along with the target product (benzhydrol, 78% yield), diphenylmethane (5%) resulted from benzophenone hydrogenation on the catalyst containing 28.3 wt % Ni at 83.1% substrate conversion. The product of benzene ring hydrogenation (cyclohexylbenzene) was present only in trace amounts.



Aniline was the only product of nitrobenzene hydrogenation on the 7% Ni/C catalyst. Under the above conditions, the reaction occurred with 100% conversion.



Nitrobenzene Aniline

As was mentioned above, the selectivity of the metal–filamentous carbon catalysts in the selective hydrogenation of unsaturated hydrocarbons is determined by the types of crystallographic faces on the surface of metal particles. The (111) face is the most active, and the total hydrogenation of dienic and acetylenic hydrocarbons into alkanes occur on it. The set of crystallographic faces on the surface of metal nanoparticles can be controlled by varying the catalyst preparation conditions and the nature of the carbon source [2–4]. We assumed that the nature of the crystallographic faces of the active component accessible to reacting molecules and the size of the metal particles have an effect on the selectivity of the catalyst in the hydrogenation of substituents at the benzene ring as well. For benzene ring activation, it is necessary that the size of the active metal particles and the geometry of the crystallographic faces on their surface correspond to the benzene ring parameters. Our experimental results confirmed this assumption. For example, the samples in which the (111) face of the nanometer-sized particles of the active component was blocked exhibited no activity in benzene hydrogenation. In our opinion, this is due to the fact that the benzene molecule is activated just on these faces, because the sizes and geometric structure of the benzene ring match well with those of the (111) face of the nickel nanoparticles. The micrographs of two samples are shown in the figure.

The above assumption is also confirmed by the fact that nickel alloys with other metals, for example, copper are inactive in benzene hydrogenation. In this case, nickel atoms are diluted with an inactive or low-active component and even the (111) face has no sites whose configuration could ensure activation of benzene molecules. Magnesium intermetallide hydrides are also inactive in this reaction, while other unsaturated compounds are hydrogenated on them even at room temperature [14]. This is explained by the specific crystal structure of these compounds: their surface also has no areas resembling the structure of the (111) face. Therefore, among the hydrogenation catalysts based on filamentous carbon, the nickel catalysts are the most promising for the selective hydrogenation of substituents in the benzene ring, because the surface of their active metal nanoparticles contains no (111) faces.

Table 2. Catalytic properties of 41.3% Ni/C in benzene hydrogenation

Reaction temperature, °C	C_6H_{12} selectivity, %	Conversion, %
100	100	32
200	100	42

Thus, we have discovered a new promising area of application of the metal–carbon catalysts based on filamentous carbon, namely, the selective hydrogenation of substituents in the benzene ring. Such catalysts can be useful in several processes of fine organic synthesis.

REFERENCES

1. Molchanov, V.V., Chesnokov, V.V., Buyanov, R.A., and Zaitseva, N.A., *Kinet. Catal.*, 1998, vol. 39, no. 3, p. 378.
2. Molchanov, V.V., Chesnokov, V.V., Buyanov, R.A., Zaitseva, N.A., Zaikovskii, V.I., Plyasova, L.M., Bukhtiyarov, V.I., Prosvirin, I.P., and Novgorodov, B.N., *Kinet. Catal.*, 1998, vol. 39, no. 3, p. 386.
3. Chesnokov, V.V., Prosvirin, I.P., Zaitseva, N.A., Zaikovskii, V.I, and Molchanov, V.V., *Kinet. Catal.*, 2002, vol. 43, no. 6, p. 838.
4. Zaitseva, N.A., Molchanov, V.V., Chesnokov, V.V., Buyanov, R.A., and Zaikovskii, V.I., *Kinet. Catal.*, 2003, vol. 44, no. 1, p. 129.
5. RF Patent 2096083, 1997.
6. RF Patent 2087187, 1997.
7. Molchanov, V.V., Chesnokov, V.V., Buyanov, R.A., Zaitseva, N.A., and Zaikovskii, V.I., *Kinet. Catal.*, 2005, vol. 46, no. 5, p. 660.
8. Maprgitfalvi, J., *Acta Chim. Hung.*, 1987, vol. 124, no. 1, p. 181.
9. RF Patent 2156654, 2000.
10. Obraztsova, I.I., Eremenko, N.K., and Velyakina, Yu.N., *Kinet. Catal.*, 2008, vol. 49, no. 3, p. 401.
11. Kuz'micheva, E.L., Nadtochii, M.L., Makhkamov, Kh.M., and Beregovykh, V.A., *Khim. Prom–t. Segodnya*, 2003, no. 4, p. 9.
12. Could, F.E., Jonson, G.S., and Ferris, A.F., *J. Org. Chem.*, 1960, vol. 25, p. 1658.
13. Ferris, A.F., Could, F.E., Jonson, G.S., and Stange, H., *J. Org. Chem.*, 1961, vol. 26, p. 2602.
14. Molchanov, V.V., Stepanov, A.A., Konstanchuk, I.G., Buyanov, R.A., Boldyrev, V.V., and Goidin, V.V., *Dokl. Akad. Nauk SSSR*, 1989, vol. 305, p. 1406.