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Effect of the Nature of Coke-Forming Species on the Crystallographic Characteristics and Catalytic Properties of Metal–Filamentous Carbon Catalysts in the Selective Hydrogenation of 1,3-Butadiene

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Abstract—The particle morphology and surface structure of nickel metal in metal–filamentous carbon catalysts were found to depend on the nature of coke-forming species used in the synthesis of catalysts. Metal carbonization with hydrocarbons that are characterized by high thermodynamic stability results in the formation of well-cut metal particles the surface of which is formed by (110) facets. Selective hydrogenation reactions of diene and acetylene hydrocarbons to olefins are typical of these catalysts. In the catalytic decomposition of hydrocarbons with relatively low thermodynamic stability, metal particles become irregular in shape, and their surface is formed by (111) facets. In this case, the reactions of full hydrogenation of olefin, diene, and acetylene hydrocarbons to corresponding alkanes take place. These data are consistent with the found dependence of the catalytic properties of catalysts on the character of the exterior faceting of active metal particles.

INTRODUCTION

It is well known that the structural characteristics of catalyst surfaces significantly affect the rates of catalytic reactions. The surface of active metal particles can be formed by differently oriented crystallographic facets depending on the conditions of synthesis. As found in a great number of studies, which were performed initially with single crystals [1, 2] and then with supported model catalysts prepared by the precipitation of metal clusters onto ultrathin oxide films [3–5], different types of crystallographic facets exhibit different catalytic properties. The crystallochemical characteristics of active metal surfaces can considerably affect not only the activity but also the selectivity of catalysts. We observed this dependence in a study of metal–carbon catalysts based on filamentous carbon in the selective hydrogenation of diene and acetylene hydrocarbons [6, 7]. A method based on the carbide cycle mechanism for the synthesis of metal–filamentous carbon catalysts allowed us to prepare the crystals of nickel or its alloys with surfaces formed by certain facets. We studied the catalytic properties of individual facets of active component particles using the selective hydrogenation reactions of 1,3-butadiene and acetylene as an example. We found that at high degrees of carbonization the (110) facets appear at the particle surface of nickel or its alloys with other metals, whereas the (111) and (100) facets are inaccessible to reacting molecules from a gas phase. The selective hydrogenation reactions of diene and acetylene hydrocarbons to olefins are typical of these catalysts. The reactions of full hydrogenation of olefin, diene, and acetylene hydrocarbons to corresponding alkanes occur at low degrees of carbonization, when all crystallographic facets of metal particles occur at the surface.

The faceting of active metal particles can be controlled by changing the degree of carbonization in samples with the use of the same coke-forming species [7]. Changing the coke-forming species noticeably changed the catalytic properties of these catalysts, all other factors being the same. On this basis, we assumed that the nature of a hydrocarbon used as the coke-forming species affects the crystallographic characteristics of the surface of active metal particles.

The aim of this work was to study the effect of the nature of coke-forming species on the faceting of an active metal formed in metal–carbon catalysts based on filamentous carbon and on the catalytic properties in the selective hydrogenation reaction of 1,3-butadiene.

EXPERIMENTAL

The procedure of catalyst preparation consisted in the production of filamentous carbon by the catalytic decomposition of hydrocarbons on iron subgroup metals or their alloys with other metals. Almost any catalysts can be used as the precursors of catalysts for hydrocarbon decomposition, in particular, spent catalysts from other processes, which contain iron subgroup metals or their alloys with other metals. Among them are bulk metal oxides; coprecipitated alumina–nickel, chromia–nickel, and magnesia–nickel catalysts; catalysts prepared by the impregnation of various sup-

Catalytic properties of samples, which were prepared from various coke-forming species, containing nickel phases with cubic (c) and (or) hexagonal (h) structures in the selective hydrogenation of 1,3-butadiene

Coke-forming species	C : Ni, g/g	Nickel structure and the type of facets at the surface	Selectivity for butenes, mol %	Reaction rate $\times 10^{-6}$, mol s^{-1} (g M)$^{-1}$
Methane	10	c (110)	97.9	19.63
Propane	14	c (110)	99.1	16.65
Benzene	10	c (111), c (100), c (110)	76.6	37.08
Hexane	1	c (111), c (100)	75.5	48.87
Hexane	10	c (111)	75.9	54.3
Butadiene	1	h (0001)	78.7	38.72
Butadiene	10	h (0001)	81.4	35.23

ports with metal salts; metal hydroxides precipitated on magnesia and alumina; and complex oxide systems prepared by mechanochemical activation.

In this study, we used the mechanochemical activation of nickel oxide and aluminum hydroxide powders in a centrifugal planet mill to prepare catalyst precursors. To synthesize metal–carbon catalysts, the resulting mixture was reduced in a flow of hydrogen directly in the McBain balance at 773–873 K. As judged from weight losses measured to within 10^{-4} g, nickel oxides were completely reduced to the metal in all of the test samples. After the reduction, an inert gas was blown through the reactor, and hydrocarbons (methane, propane, *n*-hexane, and benzene) were supplied to the reactor and decomposed at 773 K. Metal–filamentous carbon catalytic systems were formed in the course of decomposition. The synthesis of samples with the use of 1,3-butadiene as a coke-forming species was performed at 673 K in order to obtain a nickel carbide phase, which decomposes into the metal and carbon at higher temperatures in accordance with the carbide cycle mechanism. Thus, we obtained nickel particles with a hexagonal structure. The amount of carbon formed was also measured to within 10^{-4} g using the McBain balance.

The nickel and alumina contents of the catalyst precursors were 87.9 and 12.1 wt %, respectively. Samples with carbon contents of 1 and 10 g/(g Cat) were prepared from these precursors.

The electron-microscopic studies were performed on a JEM-100 CX (100 kV) instrument with a point resolution of 0.45 nm and on a JEM-200 (200 kV) instrument with a line resolution of 0.14 nm.

A URD-63 diffractometer with a graphite monochromator (CuK_α radiation) was used for X-ray diffraction (XRD) analysis and the determination of coherent-scattering regions.

The catalytic activity of samples, which were reduced with hydrogen at 673 K for 30 min, in the hydrogenation of 1,3-butadiene was studied in a flow-circulation setup at 473 K, an H_2 : 1,3-butadiene ratio of 5 : 1, and a total flow rate of 8.5 l/h; the catalyst sample weight was 0.2 g. The reaction products were analyzed by chromatography with the use of triethylene glycol *n*-butyrate on diatomaceous earth as a sorbent.

RESULTS AND DISCUSSION

A study of the catalytic properties of the prepared metal–carbon catalysts in the selective hydrogenation reaction of 1,3-butadiene demonstrated that these properties significantly depend on the nature of the coke-forming species used for the synthesis of catalysts (see table). Previously [6, 7], we reported that metal–carbon catalysts prepared by methane or propane decomposition are characterized by a considerable increase in the selectivity of olefin formation from 1,3-butadiene with increasing carbon-to-metal ratio C : M. At the ratio C : M = 5, the selectivity takes a constant value close to 100%. The replacement of methane or propane by other hydrocarbons (benzene, 1,3-butadiene, or *n*-hexane) noticeably changes the catalytic properties of the resulting catalysts. The table indicates that in all samples the selectivity for olefins was noticeably lower than that in catalysts with high C : M ratios, which were prepared by methane or propane decomposition. In each group of samples synthesized from the other coke-forming hydrocarbons, the selectivity did not increase with the degree of carbonization of the catalysts. Thus, the selectivity of catalysts with a carbon content of 1 g/(g Cat) was almost equal to the selectivity of samples with a carbon content of 10 g/(g Cat) for all coke-forming species other than methane and propane, and it was 75–85%. Differences in the selectivity within catalyst groups with equal carbon contents were also small. The catalysts synthesized with the use of benzene and 1,3-butadiene were insignificantly different in activity. The samples prepared by *n*-hexane decomposition were more active. The catalysts prepared with the use of methane and propane as coke-forming species were most closely allied in terms of selectivity. The selectivity of these samples with high C : M ratios was higher than 99%.

Thus, the nature of the coke-forming species used in the synthesis of metal–filamentous carbon catalysts noticeably affects their catalytic properties. The catalysts prepared from light alkanes (methane and propane) selectively hydrogenate diene hydrocarbons to olefins; the catalysts synthesized from higher alkanes or unsaturated hydrocarbons are less selective.

The type of facets that form the surface of metal particles in metal–filamentous carbon catalysts is a consequence of the changes that a small crystal of the metal undergoes in the course of formation and growth of filamentous carbon; these changes occur by the carbide cycle mechanism [8–10]. According to this mechanism, the catalytic decomposition of hydrocarbons with the formation of carbide-like intermediates occurs at the surface of the (100) and (110) facets of iron subgroup metals. The surface carbide serves as a source of carbon atoms, which are dissolved in the bulk of metal crystals. After supersaturation of the metal, carbon is released as a graphite phase at the (111) facet. The diffusion of carbon atoms through the bulk of the particle can be accompanied by the incorporation into the metal lattice with an increase in the lattice parameter and a weakening of interatomic bonds; this makes it possible to reconstruct the particle. It is reasonable to assume that the character of this reconstruction and, as a consequence, the crystallographic characteristics of the particle and the structure of its surface depend on the ratio between the rates of individual steps of carbonization. The rate of hydrocarbon decomposition on the surface of a catalyst with the formation of surface carbide depends on its thermodynamic stability. Among the coke-forming species used in this study (methane, propane, 1,3-butadine, *n*-hexane, and benzene), methane exhibits the highest thermodynamic stability. It was found that, because of its high thermodynamic stability, methane is different from other hydrocarbons in behavior in the carbonization of nickel. Kinetic data [11] on the decomposition of methane on alumina–nickel catalysts suggest that the activation energy of carbon formation is 75 kJ/mol over a temperature range of 798–873 K, and this is close to the published values [12–15]. On the other hand, it was found that in this case the activation energy of surface nickel carbide formation is 87 ± 12 kJ/mol [16]. These activation energies can be considered close in magnitude taking into account the differences between the procedures and conditions of determination and the properties of catalyst samples in the cited publications [6, 11]. This fact indicates that, in this case, the step of surface nickel carbide formation via the dehydrogenation of adsorbed methyl radicals is a rate-limiting step in catalyst carbonization. This fact was also supported by published data [6] on the kinetics of nickel carbide formation from methane on the (110) face of a nickel single crystal. A study of the effect of the nature of other hydrocarbons (1,3-butadiene, *n*-hexane, and benzene) on the rate of carbonization demonstrated that the replacement of 1,3-butadiene by benzene or *n*-hexane had no effect on the rate of carbon formation on nickel. According to Chesnokov and Buyanov [11], the activation energy of carbon formation from these coke-forming species at 798–873 K is 150–160 kJ/mol, which is close to the activation energy of diffusion of carbon atoms in the bulk of nickel metal. In our opinion, these facts suggest that the rate-limiting step of carbon formation from these hydrocarbons on nickel is the same, namely, the diffusion of carbon atoms through the bulk of the metal. Thus, the ratio between the rate of decomposition of a hydrocarbon on the metal surface and the rate of diffusion of the resulting carbon through the bulk of a particle depends on the nature of coke-forming species. Different ratios between the rates of these steps are responsible for different intensities of carbon fluxes through the bulk of metal particles in the samples prepared by the decomposition of different hydrocarbons. On this basis, metal particles in these catalysts would be expected to exhibit different structures. In the cases when carbon diffusion through a metal particle is the rate-limiting step of the growth of carbon filaments, the reconstruction of metal particles occurs more deeply. We might expect that (111) facets, which correspond to the most thermodynamically stable state of the system, mainly form the surface of metal particles.

We examined the catalysts by transmission electron microscopy and found that the nature of the coke-forming species used for producing the metal–filamentous carbon system noticeably affects the shape and surface structure of metal particles. Previously, it was found that nickel particles in metal–carbon catalysts prepared by methane or propane decomposition exhibited a well-faceted shape [6]. In these samples, the surface of nickel particles was formed by (100) and (110) facets at low C : Ni ratios or by only (110) facets at high ratios; in both cases, the (111) facets were blocked by carbon, and they were inaccessible to the reaction medium.

The morphology of nickel particles was noticeably changed with the use of coke-forming species such as 1,3-butadiene, benzene, and hexane. Thus, the micrographs of samples prepared from hexane (Fig. 1) at a low C : Ni ratio indicate that a number of faceted particles at the ends of carbon filaments, as well as the agglomerates of graphite-encapsulated metal particles, were formed. The faceting of metal particles at the ends of filaments impaired as the degree of carbonization increased; the agglomerates of particles with graphite shells also underwent degradation. The micrographs of samples with a high C : Ni ratio, which were prepared by benzene decomposition, primarily exhibit round-shaped polycrystalline particles. Boundaries between blocks along (111) planes can be seen in the electron micrographs of these particles (Fig. 2). Note that the number of faceted metal particles in the catalyst samples prepared by hexane decomposition was greater

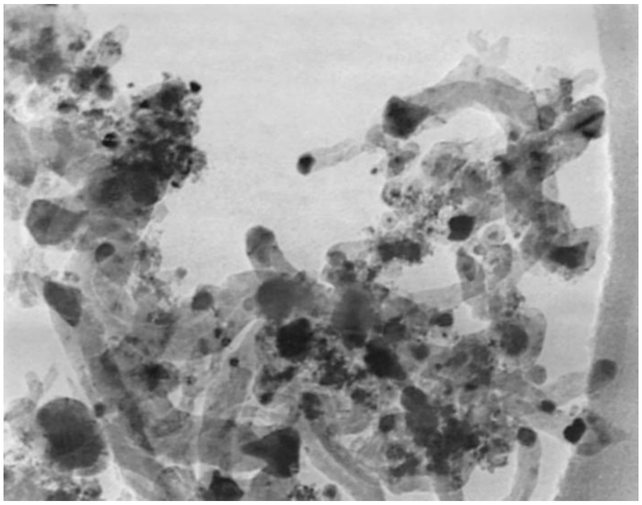

Fig. 1. Electron micrograph of a Ni/C catalyst prepared by *n*-hexane decomposition with a carbon content of 1 g/(g Cat).

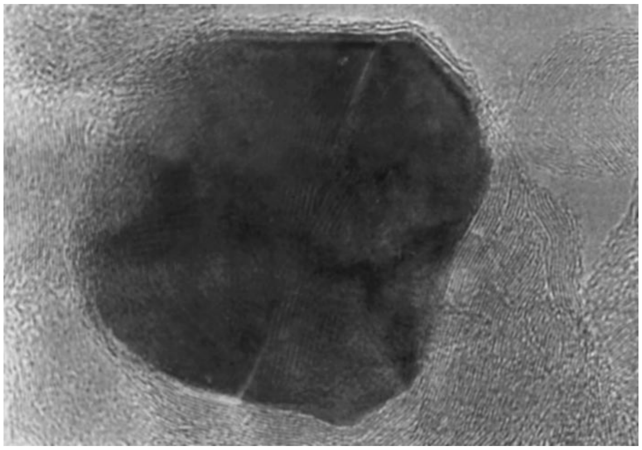

Fig. 2. Electron micrograph of a Ni/C catalyst prepared by benzene decomposition with a carbon content of 10 g/(g Cat).

than that in the samples prepared by benzene decomposition. The method of electron microdiffraction allowed us to identify facets that occur at the surface of nickel particles. We found that the surface of metal particles in the catalysts synthesized with the use of hexane is formed by (111) and (100) facets (Fig. 3). As the C : Ni ratio in the samples prepared from hexane increased, the shape of the metal particles became more round. This change in the morphology of particles was accompanied by a surface rearrangement with the formation of only faceted zones with small surface areas. The closely packed (111) planes are most typical of the surface structure of metal particles in the catalysts prepared by benzene decomposition; the (100) and (110) planes occur more rarely. Thus, the main difference in the metal surface structure between the samples prepared from benzene and hexane and the samples from methane is that, even at high C : Ni ratios, the surface of the former samples was mainly formed by (111) facets, whereas the (110) facet, which is responsible for the selective hydrogenation of diene hydrocarbons to olefins, was either completely absent or occurred in combination with (111) and (100) facets.

The synthesis of samples containing nickel with a hexagonal structure provides an additional opportunity to compare the catalytic properties of samples with different crystallochemical characteristics of active metal particles. These samples can be synthesized because, in accordance with the carbide cycle mechanism, either a metal phase or a carbide phase can be stable depending on the conditions of carbonization. The use of 1,3-butadiene as a coke-forming species and carbonization temperatures no higher than 673 K are favorable for the conversion of a carbide-like phase (Ni–C) into a true carbide phase via the intermediate formation of a carbide-like compound. In turn, this carbide is unstable; carbon and metal phases result from its decomposition. Because the carbide lattice is hexagonal, the epitaxial growth of hexagonal nickel takes place in the course of its decomposition.

According to XRD and electron-microscopic data, these metal–carbon catalysts contain either nickel metal in a hexagonal modification or nickel carbide. It is difficult to determine accurately which of these compounds is present in the samples because of the similarity of crystal lattice parameters. Because nickel carbide readily undergoes hydrogenation under the conditions used for determining the catalytic activity, it is reasonable to believe that the samples used as catalysts in 1,3-butadiene hydrogenation contained a nickel metal phase with the hexagonal structure. According to electron-microscopic data, nickel particles in the catalysts obtained by the decomposition of 1,3-butadiene exhibit a number of special features. The particles in a sample with a high C : Ni ratio are either faceted like a truncated drop or round in shape. Symmetrical filaments from 500 to 1000 Å in thickness were also detected in these catalysts; these filaments grew in contrary directions from the nickel particle [17]. The surface of cubic metal particles in these samples consisted of the particles of a hexagonal nickel carbide microphase [17].

Thus, the nature of the hydrocarbon used as the coke-forming species in the synthesis of metal–filamentous carbon catalysts can affect both the faceting of metal particles and the crystallographic characteristics. A consequence of these changes consists in differences in the catalytic properties.

Based on commonly accepted notions of a stepwise hydrogenation mechanism, facets with different crystallographic orientations can affect the selectivity of metal catalysts for several reasons. The competitive diene and olefin adsorption is one of the factors that control the selectivity of 1,3-butadiene hydrogenation for butenes. In this case, the geometry of facet surfaces that form the metal particle surface involved in catalysis plays an important role. It is well known that, as distinct from butene, the adsorption of 1,3-butadiene requires at least two surface sites [18]. As mentioned above, the metal surface accessible to a reaction medium in the samples with hexagonal nickel is mainly formed by closely packed (0001) facets. These facets are structurally similar to the (111) facet of cubic nickel; previously, we found that this facet is responsible for the occurrence of deep hydrogenation reactions. In our opinion, this circumstance governs the low selectivity of samples containing hexagonal nickel.

Another factor that controls the selectivity of hydrogenation is a kinetic factor, which is determined by the relative rates of hydrogenation of the diene and butenes and by the ratio between the rates of desorption and hydrogenation of butenes. Because it is well known that the bond strengths in hydrocarbons chemisorbed on differently oriented facets of metal crystals are different, it is believed that the above rates for these facets are different.

In our opinion, the state of hydrogen occurring in the catalyst is another important factor that affects hydrogenation selectivity. According to published data and our experimental results [7], various hydrogen species that have different energy characteristics can be formed on catalyst surfaces. Along with surface hydrogen species, hydrogen dissolved in the bulk of metal particles can be formed. Each of these hydrogen species has its particular energy characteristics to result in significant differences in catalytic properties. We studied the state of hydrogen in nickel–filamentous carbon catalysts with different sets of the crystallographic facets of nickel accessible to a reaction medium. We found that the formation of hydride hydrogen is typical of the (111) facets. This hydrogen species was not detected in the samples at the surface of which the (110) facets (which are responsible for the selective hydrogenation of diene and acetylene hydrocarbons) were mainly present. Based on these data, it is believed that the high reactivity of the hydride hydrogen species results in the occurrence of full hydrogenation to alkanes, whereas the disappearance of this species increases the selectivity of 1,3-butadiene hydrogenation to butenes. Based on the structural similarity of (0001) facets in hexagonal nickel and (111) facets in cubic nickel, it is reasonable to expect the formation hydride hydrogen species in the samples containing hexagonal nickel. This problem calls for further investigation.

Thus, we found that the type of facets (which is responsible for catalyst selectivity in the hydrogenation of diene hydrocarbons) at the surface of metal particles can be controlled by changing not only the conditions of carbonization but also the nature of coke-forming species. The nature of the coke-forming species used significantly affects the conditions of catalyst formation and changes the crystallographic characteristics of the surface, all other factors being the same. The (110) facets, which induce the hydrogenation reactions of diene and acetylene hydrocarbons to olefins, mainly form the surface of samples prepared by methane and propane decomposition with high C : Ni ratios. At the same time, the (111) facets, which are responsible for the full hydrogenation of diene and acetylene hydrocarbons to alkanes, are predominant at the surface of catalysts synthesized by the decomposition of *n*-hexane, 1,3-butadiene, and benzene.

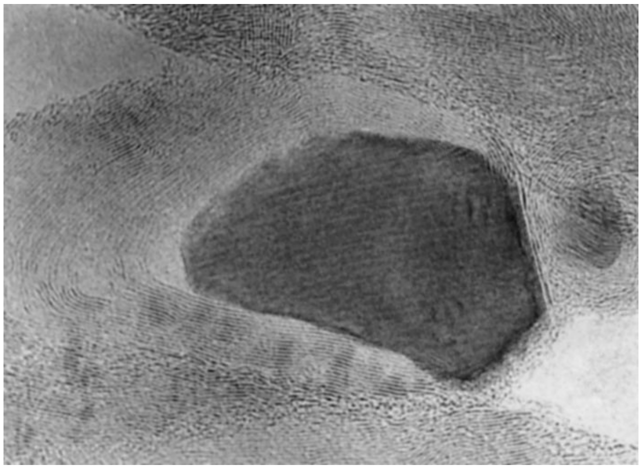

Fig. 3. Electron micrograph of a Ni/C catalyst prepared by *n*-hexane decomposition with a carbon content of 10 g/(g Cat).

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