Structure of the Active Component and Catalytic Properties of Catalysts Prepared by the Reduction of Layered Nickel Aluminosilicates

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Abstract—The reduction of Ni–Mg aluminosilicates with the amesite structure was studied using thermogravimetry, high-resolution electron microscopy, XPS, and XRD. It was found that the reduction with hydrogen at 920 K resulted in the formation of nickel particles coated with a difficult-to-reduce amorphous oxide shell. The reduced samples were incapable of chemisorbing oxygen; however, they exhibited a high adsorption capacity for hydrogen. The Ni⁰ core–oxide shell decorated particles were highly active in steam methane reforming and CO hydrogenation reactions. At the same time, they were inactive in the formation of graphite-like carbon in both methane decomposition and CO disproportionation.

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INTRODUCTION

The nature of the support and the history of the sample have a great effect on the structure and properties of catalysts containing Group VIII metal particles. Complex oxide systems containing Group VIII metal cations, which are reduced upon thermal treatment in hydrogen with the formation of metal particles, are interesting materials. In these systems, the formation of highly dispersed metal particles, which strongly interact with the support and exhibit unique catalytic properties, would be expected. Thus, the reduction of layered nickel-magnesium aluminosilicates with the structures of amesite and its polymorph (chlorite) is accompanied by the formation of dispersed nickel particles immobilized on a layered aluminosilicate substrate [1]. A special feature of these particles is their low activity in the formation of graphite-like carbon in methane and carbon monoxide atmospheres [2]. This work was devoted of the structure and chemical composition of the surface and the catalytic properties of metal nickel particles formed upon the reduction of Ni-Mg-Al aluminosilicates with the amesite structure. Thermogravimetry, high-resolution electron microscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and adsorption techniques for surface characterization were used in this study. Catalytic properties were studied in the reactions of steam methane reforming, CO hydrogenation, methane formation and thermal decomposition, and CO disproportionation.

EXPERIMENTAL

Sample Preparation and Characterization

Three samples of the Ni-Mg-amesite system with different nickel contents (hereafter, NAS1, NAS2, and NAS3) were prepared. For comparison, a Ni/MgO catalyst was also used. It was prepared by the coprecipitation of Ni²⁺ and Mg²⁺ cations from nitrate salt solutions with a mixture of NaOH and Na₂CO₃ solutions at pH 10.5 and T = 343 K. The precipitate was washed with distilled water, dried under an IR lamp, and calcined at 725-775 K in a flow of argon. To prepare Ni-Mgamesite samples, SiO₂ powder was mixed with an aqueous aluminum nitrate solution; an aqueous ammonia solution was added to pH 8, and the mixture was stirred for 30 min. The resulting gel was filtered and washed with distilled water. Magnesium hydroxide was prepared by the precipitation of Mg²⁺ cations from a magnesium nitrate solution with an aqueous KOH solution at pH 10.5-11.0 and 298-303 K. The precipitate was filtered off and washed with distilled water. The freshly prepared Mg(OH)₂ and nickel acetate were added to a silicon-aluminum-containing gel, and the resulting paste was stirred for 1 h until a homogeneous state was achieved. The resulting paste was steam heated at 575 K and 9 MPa for 4 h and then filtered off and washed with distilled water. Table 1 summarizes the composition of samples based on data obtained by atomic absorption spectrometry (AAS) and temperature-programmed reduction and oxidation (TPR-TPO) with the measurement of weight changes using a

Sampla	Catio	nic composition (1	Phase content, wt %			
Sample	Ni	Mg	Mg Al Si		NiO	Ni ⁰ *
NAS1	0.30	1.90	1.6	1.2	7.7	6.1
NAS2	0.54	1.46	2.0	1.0	13.8	11
NAS3	1.10	1.00	1.8	1.1	26.1	21
Ni/MgO	1	1	_	-	65	24

Table 1. Composition of the materials examined according to AAS, TPR-TPO, and thermogravimetric data [1]

*In reduced samples (determined from thermogravimetric data for the oxidation of the sample with atmospheric oxygen); the reduction temperature was 825 and 925 K for Ni/MgO and NAS samples, respectively.

Netzsch STA-409 instrument for thermogravimetric analysis.

The specific surface area of nickel metal in reduced samples was determined from the temperature-programmed desorption (TPD) of hydrogen in a flow of argon (1.8 l/h NTP) on heating to 673 K at a rate of 10 K/min. Before desorption, the adsorption of hydrogen onto a 50- to 100-mg sample was performed at 373 K in a flow of pure hydrogen for 12 h. The average surface area occupied by a nickel metal atom was taken equal to 6.5×10^{-2} nm² [3]. The adsorption capacity for oxygen was studied by means of N₂O decomposition at 325 K under conditions of pulsed N₂O supply and chromatographic analysis of decomposition products. Analogous measurements at 625 K allowed us to perform the titration of total nickel metal. The amount of Ni⁰ was also determined by treatment in a flow of air at 675 K and weight measurements with a Netzsch STA-409 thermal analyzer.

Phase analysis was performed on Siemens D-500 and Bruker D-8 X-ray diffractometers with the use of a CuK_{α} -radiation source (β lines were removed using a graphite monochromator).

The chemical composition of the subsurface layers of catalysts was analyzed by XPS. The XPS spectra were measured on a VG ESCALAB HP photoelectron spectrometer using Al K_{α} radiation (hv = 1486.6 eV). Samples were loaded into the vacuum chamber of the spectrometer in a flow of argon in order to prevent contact with air. The scale of binding energies (E_b) was precalibrated using the positions of Au4 $f_{7/2}$ (84.00 eV) and Cu2 $p_{3/2}$ (932.67 eV) lines in the spectra of cleaned gold and copper foils, respectively. The charging effect that appeared in the course of photoemission was taken into consideration using the internal standard technique; the C1s line of carbon ($E_b = 284.8 \text{ eV}$) was used as an internal standard. The relative concentrations of the elements in an analytical zone (the depth of analysis was 2-4 nm) were determined from the integrated intensities of photoelectron lines normalized to the corresponding atomic sensitivity factors [4]. The relative determination error for the relative concentrations of the elements was no higher than 10%. For an increase in the depth of analysis, layer-by-layer ion etching was used. The ion etching of samples was performed with the use of a VG AG-21 argon-ion gun with a beam energy of 2 keV; the rate of etching was 1-2 nm/min at a current of ~20 µA [1].

The electron-microscopic study of samples was performed using a JEOL JEM-2010 transmission electron microscope (resolution, 1.4 Å; accelerating voltage, 200 kV). The samples were applied onto perforated carbon substrates from alcohol suspensions, which were ultrasonically dispersed.

Catalytic Tests

The catalytic activity of samples in the reaction of steam methane reforming was determined in a flow-circulation fixed-bed reactor with the circulation of a gas mixture at a circulation ratio of 100. The fed mixture contained 33 vol % CH₄, 65 vol % H₂O, and 2 vol % N₂ as an internal standard. The tests were performed at atmospheric pressure over a temperature range from 823 to 1023 K. A 0.3-g catalyst sample with a particle size of 0.25–0.50 mm was used.

The catalytic activity of samples in CO hydrogenation (Fischer–Tropsch synthesis) was determined in a fixed-bed tube reactor. The feed had the composition $H_2/CO/N_2 = 6:3:1$ (by volume). The tests were performed at 483 and 503 K. A 1-g catalyst sample with a particle size of 0.25–0.50 mm was used. The samples were reduced in hydrogen at 1025 K immediately before the catalytic tests.

The catalytic activity in the reaction of methane decomposition was studied by thermogravimetry both under temperature-programmed conditions and at a constant temperature. The procedure used for the determination of catalytic activity in methane decomposition was described elsewhere [2]. The CO disproportionation reaction was also studied under temperatureprogrammed conditions using the Netzsch STA-409

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Sample	Ni ⁰ content, ^a wt %	$d_{\rm Ni}^{\rm b}$, nm	D ^{b, c} , %	$N_{\mathrm{H}_2} \times 10^5$, mol/g	$D^{\mathrm{d}},$ %	$N_{ m O} imes 10^5$, mol/g	D ^e , %	O _{ads} /H _{ads}	$S_{\rm Ni}$, m ² /g
Ni/MgO	24	29	4.2	12	5.8	27	3.30	1.13	7.1 ^{b, d, e}
NAS1	6.1	15	8.2	3.7	7.1	1.4	0.68	0.19	2.9 ^d
NAS2	11	11	10.9	12	12.7	1.6	0.42	0.07	9.4 ^d
NAS3	21	12	9.5	13	7.3	3.1	0.43	0.12	10.2 ^d

Table 2. Data on the particle size, degree of dispersion, and specific surface area of metal nickel in NAS samples and a model Ni/MgO sample obtained using XRD, the thermal desorption of hydrogen, and the decomposition of N_2O

^a From data on the titration of samples reduced at 825 (Ni/MgO) or 925 K (NAS) with atmospheric oxygen (thermogravimetry).

^b Sizes of coherent scattering domains evaluated from the integrated XRD line widths.

^c Under the assumption that the particles are cuboctahedral in shape, according to Barbier et al. [6].

^d From data on the thermal desorption of H₂ assuming that $\theta_{\rm H} = 1$. ^e From data on the adsorption of O from N₂O assuming that $\theta_{\rm O} = 2$.

instrument for thermogravimetric analysis. The sample weight was ~100 mg. The temperature was increased from 300 to 1100 K and then decreased at a rate of 4 K/min.

RESULTS AND DISCUSSION

Active Component Particle Size and Adsorption Capacity of Catalysts for Hydrogen and Oxygen

Table 2 summarizes data on the concentrations of nickel metal and the degree of dispersion (D) of a nickel metal phase in the test samples (NAS series) and a model reference sample (Ni/MgO). The structure of the samples was studied in detail previously [1, 5]. X-ray diffraction data for the Ni/MgO sample indicated that the sample before reduction was a solid solution of nickel cations in the magnesium oxide structure. The cubic unit cell parameter a = 4.198 Å was significantly smaller than that in the pure MgO oxide (4.210 Å). According to thermogravimetric and in situ XRD data, the reduction of nickel cations occurred at temperatures higher than 625 K and the degree of reduction essentially depended on temperature. Thus, 65% nickel remained in the Ni²⁺ state after reduction at 725 K. The degree of reduction reached ~45% after reduction at 825 K; this was accompanied by an increase in the particle size of Ni⁰ from 8 to 29 nm (as estimated based on XRD line broadening). According to XRD and IRspectroscopic data, NAS samples were nickel metal particles localized on the surface of a layered Ni-Mg aluminosilicate with the magnesium chlorite-vermiculite structure. The degree of nickel reduction at a reduction temperature of 923 K was close to 100%.

Table 2 summarizes data on the degree of dispersion of nickel. These data were obtained based on the sizes of coherent scattering domains evaluated from the integrated XRD line widths. Table 2 also gives the degree of dispersion of Ni⁰ evaluated from data on the adsorption capacities of samples for hydrogen and oxygen, which were experimentally determined using the thermal desorption of hydrogen and O adsorption upon N₂O decomposition, respectively.

The degree of dispersion was estimated from the particle size of Ni⁰ under the assumption that the metal particles are cuboctahedral in shape [6]:

$$D = N_{\text{surf}} / N_{\text{total}},$$

$$N_{\text{surf}} = 12 + 10m(m-2),$$

$$N_{\text{total}} = 3.33(m-1)^3 + 5(m-1)^2 + 3.67(m-1) + 1,$$

$$d = 0.27 N_{\text{total}}^{1/3}.$$

Here, N_{surf} is the number of nickel atoms on the surface of a particle, N_{total} is the total number of nickel atoms in a particle, m is the number of atoms at the edge of a cuboctahedron, and d is the particle diameter (nm).

In the evaluation of degree of dispersion from data on the thermal desorption of hydrogen, we assumed that the coverage of nickel metal with hydrogen ($\theta_{\rm H}$) was close to 1 (according to Christmann et al. [7], the degree of saturation of a nickel metal surface is $\theta_{\rm H}$ = $(0.8-0.9) \pm 20\%$). In the evaluation of the specific surface area of nickel metal, we assumed that an atom at the surface of nickel metal occupied a surface area of $6.5 \times 10^{-2} \text{ nm}^2$ [3].

The degree of dispersion estimated from XRD and hydrogen desorption data were consistent with each other for all of the samples. It is likely that the average particle size of nickel found from XRD data was somewhat overestimated because highly dispersed nickel, whose contribution to diffraction line widths was insignificant, was ignored. At the same time, highly dispersed nickel particles make a considerable contribution to the total surface area of the metal.

In the Ni/MgO sample, the surface area of nickel metal estimated from the adsorption capacity for oxygen is also consistent with data on the thermal desorp-

Treatment conditions	[Mg]/[Si]	[Ni]/[Si]	[Al]/[Si]	[O]/[Si]
Initial	1.13	0.50	1.7	7.8
775 K, Ar	0.60	0.20	1.8	5.5
925 K, H ₂	0.42	0.06	1.5	4.2
925 K, H_2 , etching with Ar^+ for 5 min	0.54	0.15	1.8	5.0
925 K, H ₂ /CO/H ₂ O, 2 MPa	0.52	0.06	1.6	4.9
925 K, H_2 /CO/ H_2 O, 2 MPa, etching with Ar ⁺ for 5 min	0.54	0.10	1.5	5.0

Table 3. Relative atomic concentrations of cations on the surface of sample NAS2, as found from XPS data

tion of H₂ and XRD data. The estimation was performed based on the assumption that the ratio of the amount of adsorbed oxygen to the amount of surface nickel metal atoms is $\theta_0 = O/Ni_s = 2$ (see publications concerning oxygen adsorption on clean nickel metal surfaces [8] and supported nickel-containing catalysts [9, 10]). Note that data obtained by Brennan et al. [8] refer to the partial pressures of O₂ lower than 13 Pa, whereas the sample examined in our study was exposed to pulses of N₂O at 0.1 MPa. In this case, the partial pressure of oxygen in decomposition products at 300– 325 K was lower than 200 Pa (the sensitivity level of our analysis for oxygen).

At the same time, the capacity of NAS samples to adsorb oxygen is very low. The decrease in the capacity to adsorb oxygen can be explained by the partial decoration of the surface of nickel metal particles with silicon oxide. Thus, for example, Delmon [11] supposed that nickel metal particles prepared by the reduction of a layered nickel silicate were partially immersed in a SiO₂ substrate. Khassin et al. [12] used high-resolution electron microscopy in order to observe complete surface coverage of Co^0 particles with silicon oxide in Co/SiO_2 samples prepared by the reduction of a layered cobalt silicate with the stevensite structure at 1025 K. It is likely that the decoration of Ni⁰ particles in NAS samples is 90-95% of the metal surface. However, to explain data on hydrogen adsorption, one has to assume that the oxide shell can activate and chemisorb hydrogen. Moreover, the chemisorption of hydrogen on the surface oxide layer is reversible.

Chemical Surface Composition of Silicon-Containing Catalysts Prepared by the Reduction of Ni–Mg Amesites (According to XPS Data)

The problem of the decoration of metal nickel particles can be clarified based on data on chemical surface compositions and high-resolution electron-microscopic data. Table 3 summarizes data on the chemical surface

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composition of sample NAS2 after various types of treatment. Figure 1 shows the Ni2*p* XPS spectra of the test samples.

The position of the Ni $2p_{3/2}$ line at 855.4–856.2 eV and the presence of pronounced satellites 6 eV higher than the main photoemission lines clearly indicate that most of the nickel occurred in the Ni²⁺ state on the sam-

Intensity



Fig. 1. Ni 2*p* XPS spectra of samples NAS2: (1) initial, (2) calcined in Ar at 925 K, (3) calcined in Ar at 925 K and reduced in H₂ at 925 K, (4) reduced at 925 K and treated in a mixture of $\overline{CO/H_2/H_2O} = 1:2:2$ at 2 MPa and 925 K, and (5) sample 4 after etching with Ar⁺ for 5 min.



Fig. 2. Electron micrographs of sample NAS2 after calcination in flowing argon at 925 K followed by reduction in H_2 at 925 K. Inset: The result of the Fourier filtration of the image of particle B.

ple surfaces [13–18] both before and after sample calcination in flowing argon. Moreover, unexpectedly, nickel almost completely occurred in the Ni²⁺ state on the sample surface even after reduction in flowing hydrogen (Fig. 1, curve 3). Only a weak shoulder observed at ~853 eV may be indicative of the presence of nickel metal on the surface or in subsurface layers. At the same time, a dramatic decrease in the Ni/Si atomic ratio upon a reductive treatment can be ascribed to the reduction of Ni²⁺ and the formation of metal particles (Table 3). The surface etching of a reduced sample with a beam of Ar⁺ for 5 min resulted in the disappearance of lines due to an oxidized state of nickel and in the appearance of an intense Ni $2p_{3/2}$ peak due to Ni⁰ at 852.8 eV [13–19]. The etching was accompanied by a considerable increase in the surface concentration of nickel (see the Ni/Si ratio in Table 3). Thus, it is believed that, as expected, the reduced sample contained nickel metal particles, however, decorated with a Ni²⁺ oxide film or particles with a characteristic thickness of at least 2 nm (the depth of XPS analysis is ~3-4 nm). Taking into account the rate of surface etching (1-2 nm/min), the average particle size of nickel metal was greater than 10 nm. However, note that the detection of nickel metal after surface etching with a beam of Ar⁺ can also be a consequence of the reduction of Ni²⁺ with a high-energy beam of argon cations [15]. The probability of this oxide reduction depends on the M–O bond energy, and it is high in the case that the standard Gibbs function of oxide formation is no higher than 250 kJ/mol on a metal basis. Kim and Winograd [15] demonstrated that the reduction of a NiO surface with a beam of Ar⁺ is possible ($\Delta_f G^0 \sim 217 \text{ kJ/mol}$), whereas the reduction of a Ni(OH)₂ surface $(\Delta_f G^0 \sim$ 445 kJ/mol) does not occur.

High-Resolution Electron-Microscopic Data on the Structure of Reduced Ni–Mg Amesite

Figure 2 shows the electron micrographs of sample NAS2 after calcination in a flow of argon at 925 K followed by reduction in H₂ at 925 K. The sample thus treated exhibited metal nickel particles distributed over the surface of a layered aluminosilicate. The electronmicroscopic data provide support for our previous conclusions [1] that the structure of a layered aluminosilicate remained unaffected in the course of calcination and reduction. In this case, the particle size of Ni⁰ varied from 4 to 8 nm, which is somewhat smaller than sizes estimated from XRD data and the thermal desorption of hydrogen. High-resolution microscopy (Fig. 2b) demonstrates that well-crystallized Ni⁰ particles (labeled B) are coated with an amorphous oxide layer (A) \sim 2 nm in thickness and the layered aluminosilicate support is well-crystallized (C). Interplanar distances in the test materials (0.20 and 0.45 nm for particle B and support C, respectively) are in good agreement with data on Ni⁰ (distance between the [111] planes of the face-centered structure of nickel metal) and chloritevermiculite structures (distance between the [020] and [110] planes, which form a pseudohexagonal structure, of the triclinic structure in accordance with JCPDS file number 34-0163). We failed to detect atomic ordering in the oxide layer (A) of a particle shown in Fig. 2, as well as in other oxide shells of this kind. Note that, in a recent study of analogous nickel metal core-oxide shell particles in finely dispersed nickel powder prepared by pulsed laser ablation followed by forced oxidation, Sakiyama et al. [19] found a layer of amorphous nickel oxide that coated a single-crystalline metal core.

Catalyst	^W SMR, mol (g Cat) ⁻¹ h ⁻¹	k, mmol (m ² Ni ⁰) ⁻¹ atm ⁻¹ h ⁻¹	TOF _{SMR} , s ⁻¹	^{<i>W</i>SMR, mol (g Cat)⁻¹ h⁻¹}	k, mmol (m ² Ni ⁰) ⁻¹ atm ⁻¹ h ⁻¹	TOF _{SMR} , s ⁻¹	^W SMR, mol (g Cat) ⁻¹ h ⁻¹	k, mmol (m ² Ni ⁰) ⁻¹ atm ⁻¹ h ⁻¹	$\mathrm{TOF}_{\mathrm{SMR}},\mathrm{s}^{-1}$	lom/L
T = 820 K			<i>T</i> = 920 K			<i>T</i> = 1020 K			$E_{ m a},{ m k}$	
Ni/MgO	0.13	0.10	1.07	0.25	0.32	3.53	0.36	1.23	13.3	88
NAS1	0.09	0.13	1.45	0.20	0.53	5.72	0.31	1.72	19.0	90
NAS2	-	-	_	_	-	_	0.31	0.68	7.44	_
NAS3	0.11	0.05	0.55	0.24	0.19	2.02	0.36	0.64	7.0	75

Table 4. Activity of the samples examined in steam methane reforming

Note: Total pressure of 0.1 MPa; molar composition of the vapor–gas mixture, $CH_4/H_2O = 0.5$; w_{SMR} is the apparent specific (per gram of catalyst) rate of methane conversion; k is the specific (per square meter of Ni⁰ surface) rate constant of the reaction; TOF_{SMR} is the turnover frequency of a single surface site (see the text).

Structure and Surface Composition of Reduced Samples Prepared by the Reduction of Ni–Mg Amesite

The above set of data obtained using XPS, electron microscopy, and the adsorption of oxygen from N_2O suggests the occurrence of a thick oxide shell around nickel metal particles. As follows from electron-microscopic and XPS data, the thickness of this shell can be ~2 nm. Indeed, in this case, reduced NAS samples should not chemisorb oxygen on the surface, which is saturated with oxygen.

The nature of the assumed oxide shell is of importance. This shell is amorphous; evidently, it cannot be simply pure NiO, which was observed previously in the case of nucleus-shell particles [19]. Indeed, the sample reduction temperature used in our experiments was sufficiently high (925 K) for the reduction of any NiO_r oxide film. Thus, it is believed that, in addition to Ni^{2+} cations, Si⁴⁺ and, probably, Al³⁺ impurity cations occurred as the constituents of the amorphous oxide shell. This hypothesis was indirectly supported by XPS data obtained in the course of the layer-by-layer analysis of NAS samples. The Mg/Si and Al/Si atomic ratios increased after sample etching with an argon ion beam (Table 3). As mentioned above, the possibility of decorating metal particles prepared by the reduction of layered silicates was repeatedly considered in the literature [11, 12]. Indirect evidence for the partial decoration of Co⁰ nanoparticles, which were prepared by the reduction of Co–Al hydrotalcites, with AlO_x oxide clusters was reported previously [20, 21].

At the same time, note that reduced NAS samples exhibited unexpected properties. It is likely that these samples did not have a free metal surface. Nevertheless, these samples were capable of activating and reversibly chemisorbing hydrogen. This can be indicative of the strong interaction of Ni²⁺ cations as oxide shell constit-

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uents with the metal core of the particle. It is also believed that, although we found the decoration of metal particles in NAS samples, these samples exhibit catalytic activity in reactions that require the activation of hydrogen and, probably, hydrocarbons.

Activity of Samples Prepared by the Reduction of Ni–Mg Amesite in the Reactions of Steam Methane Reforming and CO Hydrogenation

Table 4 summarizes the results of the catalytic tests of samples prepared by the reduction of Ni–Mg amesite at 920 K in steam methane reforming at 825–1025 K, a



Fig. 3. The temperature dependence of the turnover frequency of an active site in the reaction of steam methane reforming in Arrhenius coordinates: (*1*) Ni/MgO, (*2*) NAS1, (*3*) NAS2, (*4*) NAS3, and (*5*) published data [23].

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Catalyst	$\begin{array}{c c} w_{\text{FT}}, \\ \text{mmol} (\text{g Cat})^{-1} \text{h}^{-1} \end{array} \text{TOF}_{\text{FT}} \times 10^{-3}, \text{s}^{-1} \qquad \alpha$			$w_{\rm FT}$, mmol (g Cat) ⁻¹ h ⁻¹	$\text{TOF}_{\text{FT}} \times 10^{-3}, \text{s}^{-1}$	α	$E_{\rm a}$, kJ/mol
	Т	^r = 483 K		Т			
Ni/MgO*	_	1.60	0.50	_	2.70	0.38	70
NAS2	0.9	1.05	0.60	2.4	2.80	0.44	100
NAS3	1.1	1.20	0.54	3.1	3.30	0.40	100

Table 5. Comparison between the activities of the catalysts in CO hydrogenation

Note: 0.1 MPa; $H_2/CO = 2$: 1; CO conversion of 10–20%.

 w_{FT} is the apparent specific rate of CO conversion in the Fischer–Tropsch synthesis; TOF_{FT} is the turnover frequency of a surface site; α is the parameter of the Anderson–Schulz–Flory product distribution by number of carbon atoms; E_a is the estimated activation energy.

*Quoted from [24].

total pressure of 0.1 MPa, and the molar ratio $CH_4/H_2O = 0.5$. The specific rate constants of the reaction were calculated assuming a first-order reaction with respect to methane. For the evaluation of the turn-over frequency (TOF) of a single catalytic site (nickel

atom), we used the specific surface areas of nickel metal particles calculated from data on the thermal desorption of hydrogen. Figure 3 shows the temperature dependence of the TOF of an active site (more specifically, a hydrogen adsorption site) in steam methane



Fig. 4. Electron micrographs of (a, b) Ni/MgO and (c, d) NAS3 samples after methane decomposition at 790 K.



Fig. 5. Electron micrographs of carbon fibers formed in the course of methane decomposition (a) on NAS3 at 790 K and (b) on NAS2 at 1070 K.



Fig. 6. Electron micrographs of particles that are inactive in methane decomposition (a) on NAS3 after methane decomposition at 790 K and (b) on NAS2 after methane decomposition at 1070 K.

reforming (TOF_{SMR}) on NAS catalysts and the NiMg sample in Arrhenius coordinates. For comparison, Fig. 3 also shows experimental data for a catalyst containing 25 wt % Ni supported on MgO promoted with 6% Al (according to Rostrup-Nielsen [22, 23], sample A1). It can be seen that the specific activity of nickel in NiMg and NAS1 samples was close to published data on the activity of catalyst A1. The estimated value of the apparent activation energy of reaction on the Ni/MgO catalyst was ~90 kJ/mol (according to Rostrup-Nielsen [23], $E_a = 110$ kJ/mol for catalyst A1). For the reduced samples of Ni–Mg amesites, the apparent activation energies were close to the E_a of the Ni/MgO sample.

A comparison between the values of TOF_{SMR} showed that the specific activity of the active component in catalysts NAS2 and NAS3 was lower than the corresponding value in the Ni/MgO sample by a factor of only 1.5–2 over the test temperature range. Thus,

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decorated Ni⁰ particles exhibit catalytic activity in steam methane reforming, and this activity is comparable with the activity of nickel particles with clean surfaces.

Note that the catalytic properties of NAS samples in the reaction of CO hydrogenation (Fischer–Tropsch synthesis) at 483–503 K are little different from those observed previously [24] in Ni/MgO catalysts. As a result of the reaction, the formation of light saturated hydrocarbons to heptane was observed. The product composition was adequately described by the Anderson–Schulz–Flory distribution. Table 5 characterizes the catalytic properties of NAS catalysts in this reaction. The specific activities of NAS samples at 483 K were somewhat lower than those of Ni/MgO catalysts. The parameter α , which characterizes the selectivity of



Fig. 7. The time dependence of the rate of carbon formation in a flow of CO under temperature-programmed conditions. Samples: (1) Ni/MgO and (2) NAS2.

hydrogenaton, of the Anderson–Schulz–Flory distribution is consistent with the previously found dependence of selectivity on active metal particle size [25].

A conceivable reason for this considerable catalytic activity of fully decorated metal particles could be the degradation of an oxide shell in the reaction atmosphere. However, as mentioned above, XPS data for sample NAS2 reduced and then treated under conditions of steam methane reforming at 2 MPa suggest that the surface composition of the sample in the reaction atmosphere remained unchanged and Ni²⁺ cations remained predominant on the sample surface. The degradation of an oxide shell is even less probable under conditions of CO hydrogenation, that is, at temperatures 400 K lower than the temperature of the preceding reductive treatment. Consequently, it is the Ni⁰ core–

Table 6. Experimental rates of carbon formation in the course of CO disproportionation under temperature-programmed conditions

Sample	w _{max} , wt %/min	^{W990 K,} wt %/min	Yield of C, wt %
Ni/MgO	1.15	0.750	170
NAS1	0.30	0.025	14
NAS2	0.46	0.110	28
NAS3	0.33	0.035	16

Note: All of the data are given with reference to the weights of reduced samples.

oxide shell particles that exhibit high activity in the reaction of steam methane reforming on catalysts prepared by the reduction of Ni–Mg amesites.

Electron Microscopy of Samples after Performing Methane Decomposition

Previously [2], it was found that NAS samples were less active than the Ni/MgO model catalyst in the reaction of methane decomposition by a factor of 20–40. Khasin and Kovalenko [2], who used in situ thermogravimetry in a flow of methane, managed to find that, for the reaction of methane decomposition in the external kinetic region, the activation energy was equal to 190 ± 5 kJ/mol for both NAS samples and the Ni/MgO catalyst. However, the Ni–Mg amesite catalysts were less active than Ni/MgO in this reaction. In this work, we studied these samples after methane decomposition using high-resolution electron microscopy. It can be seen (Fig. 4) that the micrographs of Ni/MgO and NAS samples carbonized in a flow of methane were essentially different.

The carbonized Ni/MgO sample consisted of a dense ball of carbon fibers with the fishbone structure (Figs. 4a, 4b). Only a few metal particles can be visually observed in the micrographs; all of these particles were involved in the process of carbon formation. The greatest particles were coated with a thick shell of carbon; the majority of particles of size smaller than 40 nm were enclosed in a carbon fiber or arranged at its end; this is consistent with many published data [26–29].

Similar carbon fibers can also be found in carbonized samples NAS2 and NAS3 (see the survey micrograph of NAS3 in Fig. 4c, fibers are marked with arrows); however, the fibers are few. Figure 5 exemplifies these fibers. At the same time, it can clearly be seen that the vast majority of metal nickel particles was not involved in the formation of catalytic fibrous carbon. Moreover, high-resolution electron microscopy (Fig. 6) demonstrated that these metal nickel particles did not have even trace graphite structures in the nearest environment. Instead, Ni⁰ particles were coated with a layer of an amorphous phase, which was similar to that observed on reduced NAS samples (Fig. 2).

Consequently, decorated metal particles do not participate in methane decomposition, and the low activity of NAS samples in the reaction of carbon formation from methane cannot be ascribed to Ni⁰ core–oxide shell particles. It is likely that the formation of carbon can be related to the presence of an amount of ordinary undecorated Ni⁰ particles in reduced NAS samples.

Catalytic Properties of Samples Prepared by the Reduction of Ni–Mg Amesite in the Reaction of CO Disproportionation

The NAS samples were also found inactive in the reaction of CO disproportionation. Figure 7 compares the dependence of the rate of reaction on time (temper-

ature) in the course of tests performed under temperature-programmed conditions in an atmosphere of CO for Ni/MgO and NAS2 samples. The rate profile of carbon formation exhibited two maximums at 700 and 1000 K, which were attributed previously to the formation of egg-shell graphite around metal particles and carbon nanotubes, respectively [30].

It can be seen that sample NAS2 was less active and rapidly deactivated in the course of reaction. Moreover, this sample did not exhibit noticeable activity in the formation of nanotubes. The two other NAS samples were found even less active in the disproportionation of CO. Table 6 summarizes the results of tests of the samples in the disproportionation of CO. The activities of samples NAS1 and NAS3 in the region of nanotube formation (temperatures above 850 K) were lower than the activity of Ni/MgO by one order of magnitude.

CONCLUSIONS

The reduction of Ni–Mg aluminosilicates with the amesite structure with hydrogen at 920 K resulted in the formation of metal nickel particles coated with a thick amorphous oxide shell (2 nm in thickness). Because of this, reduced NAS samples cannot chemisorb oxygen; however, they exhibit high adsorption capacity for hydrogen. Correspondingly, these samples exhibit catalytic properties that are much different from those of Ni/MgO.

Thus, the Ni⁰ core–oxide shell particles are highly active in steam methane reforming. In this case, the specific activity of a single hydrogen adsorption site is no less than half of the observed activity of nickel metal in the Ni/MgO catalyst. The specific activity of the Ni⁰ core–oxide shell particles in the hydrogenation of CO is little different from the specific activity of nickel metal in the Ni/MgO catalytic system.

At the same time, the Ni⁰ core–oxide shell particles are completely inactive in the reactions of graphite-like carbon formation in both methane decomposition and CO disproportionation. The trace activity of NAS catalysts observed in these processes can be attributed to the impurities of undecorated Ni⁰. Based on the experimental data, we can conclude that metal nickel particles decorated with an oxide shell exhibit high selectivity in steam methane reforming but do not exhibit activity in the formation of graphite-like phases.

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