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Adsorption Sites of an Iron–Aluminum Catalyst for Ammonia Oxidation as Studied by the IR Spectroscopy of the Adsorbed NO Probe Molecule

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Abstract—The state of surface adsorption sites in the IK-42-1 oxide catalyst for ammonia oxidation depending on catalyst preparation conditions (the nature of raw materials and the temperature of calcination) was studied in this work with the use of the diffuse reflectance IR spectroscopy of the adsorbed NO probe molecule. Hematite, which was prepared by a sulfate or chloride technology, was used as the starting raw material; Al_2O_3 binding agents were prepared by the reprecipitation or hydration of thermally activated gibbsite; and acetic or nitric acid was used as an electrolyte. The samples were calcined at 900–1000°C. It was found that mono- and dinitrosyl complexes with reduced coordinatively unsaturated Fe^{2+} cations and nitrite–nitrate complexes were formed upon the adsorption of NO on the catalyst surface (regardless of the catalyst preparation conditions). The samples differed in the amount and degree of coordinative unsaturation of adsorption sites depending on the preparation conditions. It was concluded that the most coordinatively unsaturated Fe^{2+} adsorption sites observed were formed on the surface of a solid solution of iron cations in aluminum oxide, which was formed in the course of catalyst preparation. It was found that an increase in the catalyst calcination temperature resulted in a decrease in the number of coordinatively unsaturated adsorption sites, which correlated with the observed decrease in the yield of NO. This correlation had the shape of a saturation curve, which can reflect the occurrence of a reaction in the diffusion mode at high degrees of conversion for the majority of catalysts.

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INTRODUCTION

Mixing followed by the extrusion molding of catalyst pastes is one of the most commonly used methods for the preparation of granular (including honeycomb monolith) oxide catalysts/supports; this method is attractive in terms of simplicity and low-waste production [1–3]. The molded pastes were prepared by mixing an active oxide and a binding agent in the presence of electrolytes, surfactants, and other additives (such as thermal stabilizers, pore-forming materials, reinforcing agents, and structure-forming agents) [4, 5]. In this case, the main properties of the catalyst (activity in the target process, strength, stability, etc.) depended on catalyst preparation conditions, including the chosen starting raw materials [4, 6].

We previously studied the effect of preparation conditions (starting raw materials and calcination temperature) on the properties (strength, pore structure, and activity) of iron–aluminum oxide catalyst granules prepared by extrusion molding for ammonia oxidation [6]. The catalyst prepared from hematite obtained by a chlorine technology was characterized by a higher activity (as compared with hematite obtained by a sulfate technology) after thermal treatment at 900°C. In the general case, an increase in the degree of interaction between catalyst components, which was observed based on a change in the hematite lattice parameter as the calcination temperature was increased to 1000°C (this change reflects the insertion of aluminum cations into the hematite lattice), resulted in a decrease in the yield of NO with retention of a 100% ammonia conversion. In this case, an increase in the yield of NO on granules calcined at 950°C was observed for sulfate hematite with a simultaneous increase in the degree of interaction with calcination temperature. The observed increase in the catalyst selectivity can be due to the states of surface adsorption sites; this phenomenon should also be studied.

Therefore, the aim of this work was to study the surface properties of the IK-42-1 iron–aluminum catalyst for ammonia oxidation depending on catalyst preparation conditions (the nature of starting raw materials and the temperature of calcination) with the use of the IR spectroscopy of the adsorbed NO probe molecule.

EXPERIMENTAL

In this study, the following two iron oxide samples were used as starting reagents: KMK (“chlorine”) from the Kuznetsk Metallurgical Combine (Novokuznetsk), which was prepared by the thermal decomposition of iron(II) chloride in spray columns, and MZKhR (“sulfate") from OAO Mikhailovskii Zavod Khimreaktivov (Malinovoe Ozero, Altai Territory), which was prepared by coprecipitation using a sulfate technology. The following four samples were used as binding agents: GATKhA aluminum hydroxide prepared at AO Katalizator (Novosibirsk) by the hydration of thermally activated gibbsite from OAO Achinskii Glinozemnyi Kombinat; GAP pseudoboehmite from OAO Angarskii Zavod Katalizatorov i Organicheskogo Sinteza; and bayerite (BA) and amorphous hydroxide (AM) prepared by the hydration of thermally activated gibbsite at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences.

The catalysts were prepared by the extrusion molding of a catalyst paste as rods or honeycomb monoliths as hexagonal prisms (a side of 2 cm) penetrated by unidirectional triangle channels (a wall thickness of 1 mm and a channel side of 2 mm). For this purpose, 80 g of iron oxide, a binding agent (which gave 15 g of aluminum oxide upon calcination), and 5 g of aluminosilicate fibers were placed in a 150-ml Z-shaped mixer. The powders were homogenized for 20 min; next, the solutions of acetic or nitric acid and a surfactant were added, and the contents were stirred to obtain a plastic paste. The resulting paste was placed in a syringe and molded as honeycomb monoliths or rods; then, they were dried at room temperature for a day and calcined in air at 900, 950, and 1000°C for 4 h.

The diffuse reflectance IR spectra of catalyst powders were measured on a Shimadzu 8300 FTIR spectrometer using a DRS 8000 Shimadzu diffuse reflectance accessory in the region of 6000–400 cm^{-1} with a resolution of 4 cm^{-1} and the accumulation of 100 spectra. The spectra were measured before and after NO adsorption. The catalyst powder (~0.25 g) was placed in a cell and evacuated at 450°C for 1.5 h. The adsorption of NO was performed at room temperature and a pressure of 20 Torr. We assumed that the integrated intensity of absorption bands in the spectra of adsorbed NO plotted on the Kubelka–Munk scale $F(R)$ was proportional to the concentration of adsorbed complexes per unit weight of the catalyst because we preliminarily found a weak dependence of the scattering coefficients of the samples on the sample calcination temperatures (based on the intensity of reflection over the range of 4000–6000 cm^{-1}).

The catalytic activity (yield of NO, %) in the ammonia oxidation reaction (at 100% conversion) was determined in the flow mode at atmospheric pressure and 900°C. For this purpose, 15 cm^3 of a catalyst fraction with a size of 2–3 mm was loaded in a quartz reactor 22 mm in diameter, and a reaction mixture (5% ammonia in air) preheated to 450°C was passed at a velocity of 1.2 m/s. After the catalyst reached a temperature of 900°C, it was exposed to the reaction mixture for 0.5 h or longer. Thereafter, the nitroso gases (NO and NO_2) were analyzed with the use of a Quintox KM9006 analyzer (relative measurement error of 5%) at regular 15-min intervals for 1–2 h (for this purpose, the reaction mixture was cooled and diluted). The arithmetic mean of three measurements with a discrepancy between them of no greater than 5% was taken as the test result.

RESULTS AND DISCUSSION

The reaction scheme of the interaction of nitrogen oxide with the surface of iron oxide can be described by the following equations [7–10]:

NO adsorption at coordinatively unsaturated Fe^{3+} cations (initially occurring or formed upon vacuum treatment)

$$O_5-Fe^{3+} + NO \longrightarrow O_5Fe^{3+}-NO,\ \nu = 1940\ cm^{-1}; \tag{I}$$

interaction of NO with oxygen from the coordination sphere of Fe^{3+} cations

$$O_6-Fe^{3+} + NO \longrightarrow O_5Fe^{3+}-(NO_2),\ \nu = 1600\ cm^{-1}; \tag{II}$$

reduction of iron cations

$$\begin{gathered} O_6-Fe^{3+} + NO \longrightarrow O_5Fe^{2+} + NO_2, \\ O_5-Fe^{2+} + NO \longrightarrow O_{5-x}Fe^{2+} + NO_2, \end{gathered} \tag{III}$$

where $5 - x$ refers to the localization of iron at defect surface sites;

NO adsorption at reduced iron cations

$$\begin{gathered} O_5Fe^{2+} + NO \longrightarrow O_5Fe^{2+}-NO, \\ \nu = 1900\text{–}1850\ cm^{-1}, \\ 2O_{5-x}Fe^{2+} + NO \longrightarrow 2O_{5-x}Fe^{2+}-NO, \\ \nu = 1800\ cm^{-1}, \\ O_5Fe^{2+}-(NO) + NO \longrightarrow O_5Fe^{2+}-(NO)_2, \\ \nu = 1910 \text{ and } 1820\ cm^{-1}, \\ O_{5-x}Fe^{2+}-(NO) + NO \longrightarrow O_{5-x}Fe^{2+}-(NO)_2, \\ \nu = 1840\ cm^{-1},\ 1750\ cm^{-1}, \\ O_5Fe^{2+}-(NO) + NO \longrightarrow O_6Fe^{3+}-N_2O, \\ \nu = 2235\ cm^{-1}; \end{gathered} \tag{IV}$$

interaction of the resulting NO_2 with iron cations and oxygen from the coordination sphere

$$O_5Fe^{2+} + NO_2 \longrightarrow O_5Fe^{2+}-NO_2,\ \nu < 1600\ cm^{-1}. \tag{V}$$

Figures 1–3 show the spectra of NO adsorbed on catalyst samples prepared by various procedures, depending on the nature of the raw materials used and the temperature of calcination.

The following conclusions can be drawn taking into consideration all of the processes that can occur on NO adsorption expressed in Eqs. (I)–(V) and based on generally accepted published data on the absorption frequencies of the corresponding complexes:

Absorption bands in the regions of 1200–1600 and 1700–1900 cm^{-1} were observed upon the adsorption of

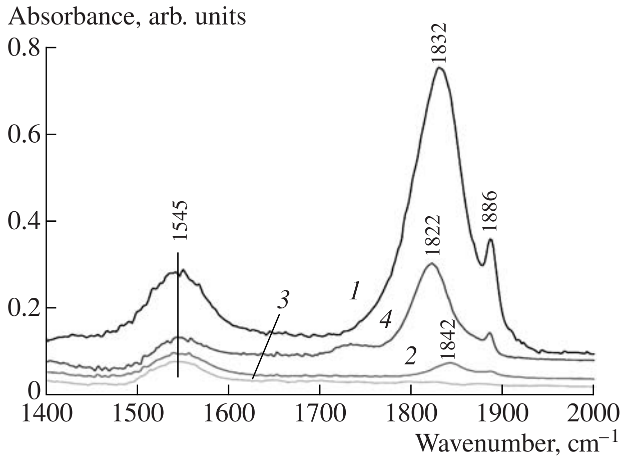

Fig. 1. Spectra of NO adsorbed on the samples of (*1*) "sulfate" iron oxide, (*2*) "chlorine" iron oxide, (*3*) "chlorine" iron oxide after additional calcination at 900°C, and (*4*) "chlorine" iron oxide after washing with water.

NO on the test samples. These bands can be attributed to the surface nitrate–nitrite complexes (absorption bands below 1600 cm^{-1}) and the complexes of NO adsorbed at coordinatively unsaturated reduced Fe^{2+} cations (absorption bands above 1700 cm^{-1}). The observed difference between the spectral manifestations of adsorbed NO complexes (the positions of absorption band maximums) for differently prepared samples can reflect different degrees of the coordinative saturation of Fe^{2+} cations. (For example, it is likely that the absorption bands of the adsorbed NO molecule at 1885 and 1832 cm^{-1} were due to the O_5Fe^{2+}–NO and $O_{5-x}Fe^{2+}$–NO complexes, respectively.) Based on the experimental spectra, we cannot exclude the adsorption of NO as not only mono- but also dinitrosyls because the observed absorption bands with a maximum at about 1815 cm^{-1} were broadened. Because absorption bands were absent from the region above 1940 cm^{-1}, we can state that complexes of adsorbed NO with trivalent iron cations and adsorbed nitrous oxide complexes were not formed.

The observed spectra of adsorbed NO complexes can reflect the interaction of NO with Fe^{3+} cations (in accordance with Eq. (II)), the reduction of the surface and the formation of NO_2 upon the adsorption of NO (in accordance with Eq. (III)), and the subsequent adsorption of NO (Eq. (IV)) and NO_2 (Eq. (V)) on the resulting coordinatively unsaturated sites. In addition, a portion of the coordinatively unsaturated sites can be due to the defect nature of the initial samples, or it can be formed in the course of vacuum treatment. The table summarizes data on the observed absorption bands and the quantitative relation between adsorbed NO species for all of the test samples.

Adsorption of NO on Hematite Prepared by Various Procedures

Upon the adsorption of NO on the "sulfate" iron oxide, absorption bands at 1885 and 1832 cm^{-1} were observed (the latter was more intense), as well as an absorption band at 1545 cm^{-1} (Fig. 1). The absorption band at 1885 cm^{-1} can be attributed to NO adsorbed at coordinatively unsaturated cations (O_{5-x})Fe^{2+}–NO, whereas it is likely that the absorption band at 1832 cm^{-1} can be ascribed to O_5Fe^{2+}–NO complexes with a nearly tetracoordinated state. The absorption band at 1545 cm^{-1} corresponds to the O_5Fe^{2+}–NO_2 complex, which resulted from the interaction of NO with the catalyst surface. The low intensity of this absorption band may suggest that surface reduction with NO occurred to a small degree and the reduced sites of NO adsorption, which are characterized by absorption bands at 1885

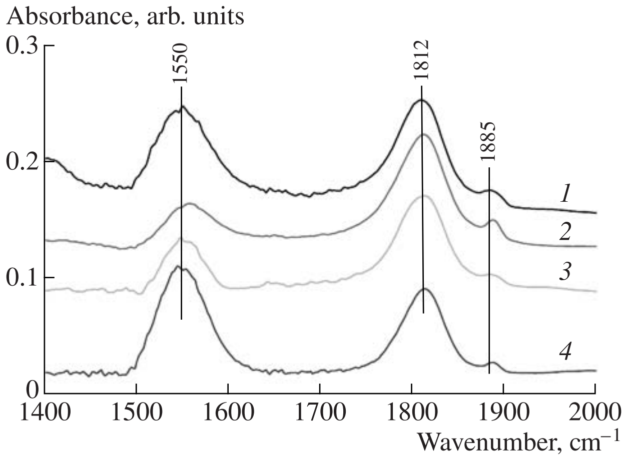

Fig. 2. Spectra of NO adsorbed on the samples of catalysts prepared with the "chlorine" iron oxide and various binding agents [(*1*, *3*) GATKhA and (*2*, *4*) GAP] and electrolytes [(*1*, *2*) acetic acid and (*3*, *4*) nitric acid].

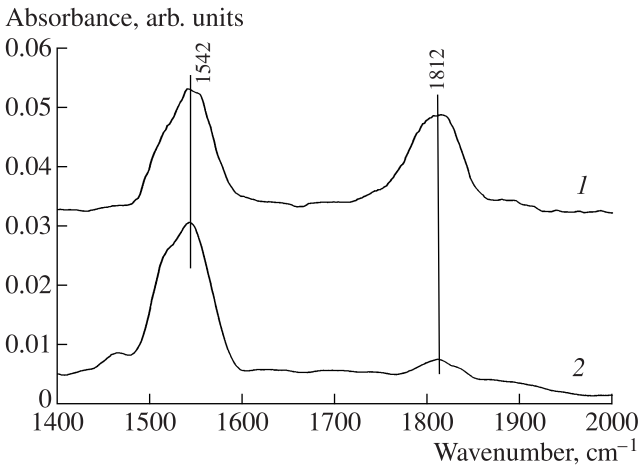

Fig. 3. Spectra of NO adsorbed on sample no. 6 (see table) (MZKhR + AM) calcined at (*1*) 900 and (*2*) 1000°C.

Integrated intensities of absorption bands due to nitrite–nitrate and nitrosyl complexes formed on the surfaces of the test catalysts upon the adsorption of the NO probe molecule depending on catalyst calcination temperature (T_{calcin}) and the nature of test raw materials (according to diffuse reflectance spectroscopic data)

Sample no.	Preparation conditions		Characteristics of the catalyst 80%Fe_2O_3 + 15%Al_2O_3 + 5%(Al, Si)O_2				
	raw materials	T_{calcin}, °C	S_{sp}, m^2/g	NO* (absorption bands at 1810–1850 cm^{-1})	NO_x^* (absorption bands at 1540 cm^{-1})	NO*/NO_x^*	yield of NO, % [6]
1	KMK + GAP	900	11	0.14	0.89	0.16	92
		950	5	0.075	0.54	0.14	85
		1000	3.4	0.07	0.40	0.26	77
2	KMK + GATKhA	900	9.1	2.5	0.88	2.8	92
		950	4.1	0.16	0.36	0.4	84
		1000	2	0.024	0.1	0.24	56
3	MZKhR + GAP	900	10	0.74	0.54	1.4	86
		950	4.6	0.32	0.45	0.7	90
		1000	2.8	0.12	0.30	0.4	82
4	MZKhR + GATKhA	900	12	1.7	1.0	1.7	91
		950	4.8	0.17	0.3	0.7	93
		1000	4.1	0.08	0.40	0.2	97
5	MZKhR + BA	900	8.4	0.45	0.64	0.7	94
		950	4.8	0.70	0.75	0.9	89
		1000	3.0	0.31	0.4	0.8	82
6	MZKhR + AM	900	7.2	0.20	0.27	0.7	90
		950	3.2	0.20	0.45	0.4	92
		1000	2.4	0.048	0.50	0.1	81

* Integrated absorption band intensities (proportional to the concentration of adsorbed complexes).

and 1832 cm^{-1}, were formed in the course of treatment; this can reflect the defect nature of the given oxide.

The absorption bands of NO adsorbed on the “chlorine” iron oxide were much less intense (by an order of magnitude) than those in the case of the “sulfate” oxide at close specific surface areas of the samples. In this case, absorption bands were observed at 1842, 1885, and 1545 cm^{-1}. The low intensity of the absorption bands at 1842 and 1885 cm^{-1} suggests a much lower (than in the sulfate sample) concentration of reduced coordinatively unsaturated sites on the surface of the given oxide and a higher degree of the coordinative unsaturation of surface adsorption sites. A reason for this may be the lower reducibility of the oxide in the course of treatment and the lower reactivity toward the NO probe molecule, probably because of the stabilization of active sites by chloride anions present in the oxide.

After sample calcination at 900°C, which facilitated the removal of residual chloride anions, the intensity of absorption bands at 1842 and 1885 cm^{-1} decreased rather than increased (whereas the absorption band intensity at 1545 cm^{-1} remained unchanged). This fact suggests that the annealing of parent defects occurred simultaneously with the removal of chloride anions and the formation of a still less reactive surface. On the contrary, the washing of samples caused an increase in the intensity of absorption bands due to the mononitrosyl complexes of adsorbed NO (absorption bands at 1842 and 1885 cm^{-1}) almost to the level of the sulfate sample.

Thus, the lower concentration of coordinatively unsaturated adsorption sites on the surface of the “chlorine” iron oxide was due to their blocking by chloride anions. Washing made the sample similar to the sulfate sample. The calcination of this catalyst in air, which also resulted in the removal of chloride anions, resulted in a decrease in the reactivity of the oxide surface upon the interaction with NO; this was likely due to the annealing of defects.

Adsorption of NO on Catalysts Prepared by Various Procedures

The catalysts based on the “chlorine” oxide prepared with various binding agents (GATKhA and GAP) and electrolytes (nitric and acetic acids) after calcination at 900°C had no considerable differences in the positions of absorption bands in the spectra of adsorbed

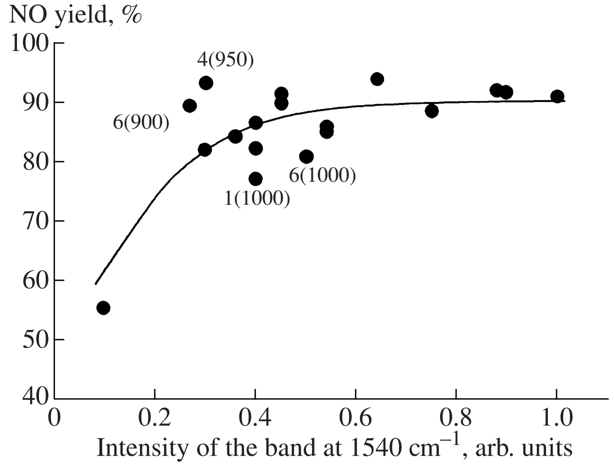

Fig. 4. Dependence of the yield of NO in the oxidation of ammonia on the intensity of the absorption band at 1540 cm^{-1} for various samples (see the table).

NO. As in the case of the parent oxide, absorption bands at 1540 and 1885 cm^{-1} were detected. However, an absorption band at ~1810 cm^{-1} was observed in place of the absorption band at 1842 cm^{-1}, and the intensity of the former was much higher than that of the absorption band at 1842 cm^{-1} measured on iron oxide (Figs. 1, 2). Note that considerable changes in the absorption band intensity at 1540 cm^{-1} did not occur in this case.

A shift of the absorption band at 1840 cm^{-1} toward lower frequencies (1810 cm^{-1}) may reflect the formation of even more coordinatively unsaturated Fe^{2+} sites (up to the formation of a tetracoordinated state or the clusters of reduced Fe^{2+} cations) on the catalyst surface in the course of training or because of a change in the defect structure unlike the surface of iron oxide. It is likely that these low-coordination iron cations can be formed at iron cations as the constituents of a solid solution in aluminum oxide. Similar absorption bands were also observed upon the adsorption of NO on iron oxide supported onto an Al_2O_3 carrier [10]. It is less probable that the observed sites can be ascribed to a solid solution of aluminum in iron oxide and, correspondingly, it is more reactive than iron oxide because of an increase in the Fe–O bond strength in it [6], as evidenced by a decrease in the lattice parameter.

Thus, in the iron–aluminum catalysts based on the "chlorine" iron oxide (compared with the parent oxide), new coordinatively unsaturated adsorption sites probably appear on the surface because of the formation of a highly dispersed solid solution of iron cations in aluminum oxide. Against the background of a higher intensity line at 1810 cm^{-1}, absorption bands due to coordinatively unsaturated iron cations on the surface of the iron oxide phase (1840 cm^{-1}) cannot be detected, or, which is very likely, these sites related to the outcrop of defects at the surface are decorated with highly dispersed alumina particles [11]. This means that not only the coordinatively unsaturated sites of a hematite phase but also Fe^{2+} sites in a nearly tetracoordinated state (an absorption band at 1810 cm^{-1}), which are formed at iron cations as a constituent of the solid solution in alumina, participate in the reaction of ammonia oxidation on the surface of an iron–aluminum catalyst.

It is of interest that the positions and intensities of absorption bands due to adsorbed NO became similar for catalysts prepared from various iron oxides and binders. This allowed us to correlate these data with similar data on the activity of catalysts. However, note that, unlike the "chlorine" iron oxide, the addition of binding agents to the "sulfate" iron oxide resulted in a decrease in the absorption band intensities of the nitrate and nitrosyl complexes of adsorbed NO. This fact supports the previous hypothesis that a portion of active sites was blocked by aluminum oxide on the iron oxide surface and additional coordinatively unsaturated sites were formed at iron cations as the constituents of a solid solution in alumina on the catalyst surface (the absorption band at 1810 cm^{-1}). This solution can be formed because of the partial dissolution of iron oxide during the preparation of the catalyst paste. Note that, in the case of catalysts based on the "chlorine" iron (T_{calcin} = 900°C), the intensity of absorption bands due to coordinatively unsaturated sites was somewhat higher than that in the catalysts based on the "sulfate" support; this can reflect the higher selectivity of this catalyst (table, catalysts 2 (900) and 4 (900)).

Figure 3 shows the spectra of adsorbed NO on iron oxide catalysts depending on calcination temperature. An increase in calcination temperature, which caused a decrease in the yield of nitrogen monoxide, also resulted in a decrease in the intensity of absorption bands due to adsorbed NO and nitrite–nitrates. As in the case of iron oxide, this reflects a decrease in the number of catalytically active adsorption sites on the surface of samples because of the occurrence of agglomeration processes and annealing on defects. Moreover, the formation of a solid solution of aluminum in iron oxide, which was observed as the calcination temperature was increased, may also decrease the reactivity of catalyst surfaces. Thus, we can generally state that the sample characterized by a higher concentration of coordinatively unsaturated adsorption sites or a higher reactivity toward NO (i.e., a higher concentration of nitrite complexes) exhibits higher selectivity in the reaction of ammonia oxidation (see the table).

Figure 4 shows the dependence of selectivity (the yield of NO) on the intensity of the absorption band at 1540 cm^{-1} due to surface nitrate fragments. It can be seen that, indeed, an increase in the selectivity was observed in all of the samples as the intensity of the above band increased. Samples 6 (900) and 4 (950) with higher activities and samples 1 (1000) and 6 (1000) with lower activities somewhat deviated from the common dependence. In addition, the spectra of samples 1 (1000) and 6 (1000) exhibited lower absorption band intensities at 1815 cm^{-1} (and, correspondingly, lower NO/NO$_x$ ratios). On the contrary, the spectra of samples 6 (900) and 4 (950) with higher activities were characterized by the more pronounced appearance of absorption bands in the region of 1880–1890 cm^{-1}. The found correlation between the yield of nitrogen monoxide in the oxidation of ammonia and the amount of nitrate complexes formed upon NO adsorption had the shape of a saturation curve, which can reflect the occurrence of a reaction in a diffusion mode at high degrees of conversion for the majority of catalysts.

The experimental data indicate that the process selectivity depends mainly on the occurrence of coordinatively unsaturated adsorption sites characterized by surface nitrate complexes (with an absorption band at 1540 cm^{-1}) on catalyst surfaces. Surface nitrosyl complexes (with absorption bands at 1810–1890 cm^{-1}) can exert an additional effect on selectivity. Thus, higher selectivity was observed in the presence of absorption bands due to nitrosyl complexes adsorbed at O_5Fe^{2+} in the hematite structure (absorption bands at 1890 cm^{-1}) in the spectra. On the contrary, the lower intensity of absorption bands at 1810–1815 cm^{-1} in the region of the spectral manifestation of nitrosyl structures correlated with a decrease in the selectivity. To establish quantitative relationships between selectivity and ratios between various coordinatively unsaturated Fe^{2+} and Fe^{3+} sites, which adsorb NO and NO_2, respectively, detailed studies should be performed. In particular, activity in the kinetic region should be measured and the amount of surface complexes should be determined using quantitative IR-spectroscopic techniques (with the use of transmission spectroscopy). In general, the experimental data obtained in this work are consistent with published data on the surface properties of iron oxide studied by the IR spectroscopy of adsorbed NO and the mechanism of ammonia oxidation on oxide catalysts (including studies performed with the use of diffuse reflectance spectroscopy). From these data, it follows that ammonia oxidation products in the gas phase are formed through the formation of oxidation products, including the surface complexes of NO, N_2O, and NO_3, on the surface of an oxide catalyst by interaction with ammonia (in the presence or absence of oxygen) [12–15].

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