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ESR and TPD Study of the Interaction of Nitromethane and Ammonia with HZSM-5 and CuZSM-5 Zeolites

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Abstract—The properties of complexes formed on HZSM-5 and CuZSM-5 zeolites in the course of ammonia and nitromethane adsorption are studied. Ammonia adsorbs on CuZSM-5 and forms two species, which decompose at different temperatures T_{dec}. One is due to the formation of the $Cu^{2+}(NH_3)_4$ complex (T_{dec} = 450 K), and the other is assigned to ammonia adsorbed on copper(II) compounds, $Cu^{2+}O^-$ and $Cu^{2+}–O^{2-}–Cu^{2+}$, or CuO clusters (T_{dec} = 650–750 K). Ammonia adsorption on Cu^+ and Cu^0 is negligible compared with that on the Brönsted acid sites and copper(II). Nitromethane adsorbed on HZSM-5 and CuZSM-5 at 400–500 K transforms into a series of products including ammonia. Ammonia also forms complexes with the Brönsted acid sites and copper(II) similar to those formed in the course of adsorption from the gas phase, but the $Cu^{2+}(NH_3)_4$ complexes on CuZSM-5 are not observed. Possible structures of ammonia and nitromethane complexes on Brönsted acid sites and the Cu^{2+} cations in zeolite channels are discussed. The role of these complexes in selective NO_x reduction by hydrocarbons over the zeolites is considered in connection with their thermal stability.

INTRODUCTION

Nitroxyl–hydrocarbon complexes play an important role in selective catalytic NO_x reduction by olefins on CuZSM-5 [1] or reduction by alkanes on CoZSM-5 in excess oxygen [2]. Adsorbed nitromethane can be such a complex. It is believed to transform on the zeolite to form HNCO or NH_3, which interact with NO_x to form N_2 [3–5].

To verify the reaction mechanism, we studied earlier [6] the adsorption and conversion of nitromethane and deuteroacetonitrile over HZSM-5, CoZSM-5, and CuZSM-5 catalysts by IR spectroscopy. The effect of the cation nature on the pathways of the conversion of these compounds was found. The mechanism was proposed to explain the selectivity of these catalysts.

This work continues our studies on the adsorption and conversions of nitromethane and ammonia and possible intermediates in NO_x reduction over zeolites HZSM-5 and CuZSM-5. Here, we use ESR and TPD techniques.

EXPERIMENTAL

HZSM-5 and 2.85% CuZSM-5 (SiO_2/Al_2O_3 = 40) zeolites were studied. The preparation of samples, the state of copper, and the ESR technique were described in detail in [7]. Changes in the state of Cu^{2+} cations after various treatments were monitored by ESR. Spectra were recorded at room temperature. To estimate the amount of Cu^{2+} cations, ESR spectra were integrated twice and compared with that of the $CuSO_4 \cdot 5H_2O$ standard with a known concentration of copper ions; the spectrum of the standard was processed as the ESR spectrum of the test sample. The coordination of the Cu^{2+} cations was determined from the parameters of a g tensor and the hyperfine structure (hfs) constant.

ESR and TPD measurements were carried out using a weighed sample (50 mg) in an ESR ampule in a vacuum. The samples were preliminarily evacuated to 1×10^{-4} Pa at 970 K and heated at this temperature in oxygen at a pressure of 2×10^2 Pa for 1 h. Then, oxygen was removed by evacuation to 1×10^{-4} Pa, and the sample was cooled to room temperature. After this treatment, the gas under study was adsorbed at a pressure of 2×10^2 Pa and 293 K for 5 min and then evacuated for 20 min. TPD spectra were recorded at a heating rate of 12 K/min under continuous evacuation. Similar studies were carried out with CuZSM-5 samples reduced with hydrogen at a pressure of 5×10^2 Pa for 1 h at T = 970 K after their preliminary oxidation by O_2.

Desorption spectra (a pressure of desorbed gas as a function of the temperature of the sample) were recorded using the Pirani manometer [8]. Desorption products were analyzed using an MX-7303 mass spectrometer with sampling through a capillary. Ammonia was registered by ionic peaks of 16 and 17 amu, whose ratio was ~1, and nitromethane was registered by the fragment masses of 15 and 30 amu. The amount of desorbed molecules was estimated in a repeated TPD run from a pressure of the gas evolved into an ampule/reac-

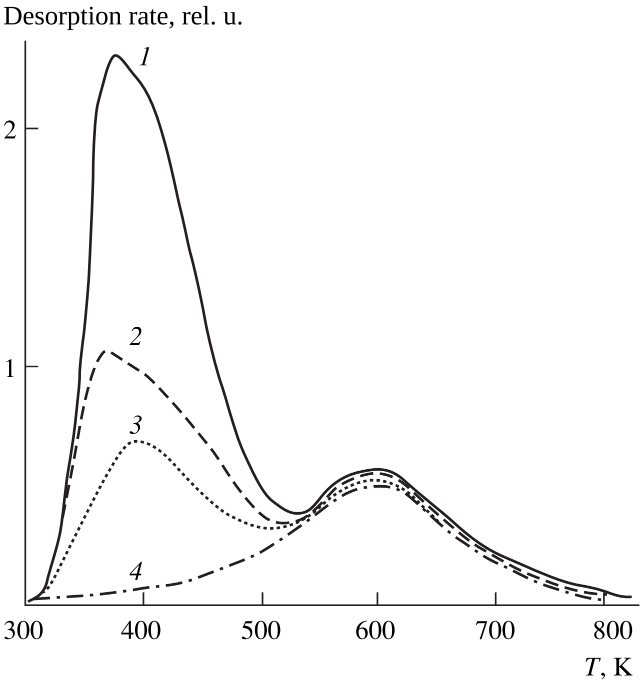

Fig. 1. TPD spectra after ammonia adsorption on HZSM-5 for 5 min at 300 K and (*1*) 2×10^2, (*2*) 1×10^2, and (*3*) 50 Pa and evacuation of the sample after adsorption for τ = 20 min: (*4*) 2×10^2 Pa and τ = 60 min.

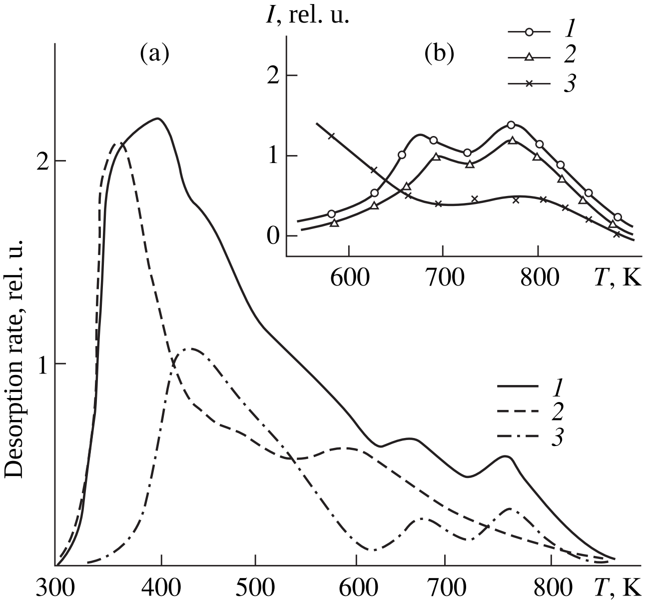

Fig. 2. (a) TPD spectra after ammonia adsorption for 5 min at 300 K, $P = 2 \times 10^2$ Pa and subsequent evacuation for 20 min of the sample of 2.86% CuZSM-5: (*1*) preliminarily oxidized and (*2*) reduced; (*3*) was obtained by subtraction of spectrum *2* from spectrum *1*; (b) intensity (*I*) of the lines in the mass spectrum during TPD after ammonia adsorption ($P = 2 \times 10^2$ Pa, τ = 20 min) on oxidized CuZSM-5: (*1*) 28 amu (N_2), (*2*) 18 amu (H_2O), (*3*) 17 amu (NH_3).

tor without evacuation. The uncertainty in these measurements for the NH_3 desorption was better than 20%.

Ammonia and CH_3NO_2 (chemical purity grade) were additionally purified before admission to a sample by double freezing in a trap with liquid nitrogen in a vacuum.

RESULTS

1. Temperature-Programmed Ammonia Desorption from HZSM-5 and CuZSM-5 Zeolites

Figure 1 presents the thermal desorption spectra from HZSM-5 zeolite after NH_3 adsorption at various pressures and periods of subsequent evacuation (τ). As can be seen, after gas adsorption at $P > 50$ Pa, the spectra consist of two peaks with maxima at T_{max} = 370 and 610 K. When a pressure of the adsorbed gas was decreased from 2×10^2 to 50 Pa at τ = 20 min, the first peak disappeared, but the intensity of the second peak did not change. The amount of desorbed gas decreased from 6×10^{20} to 1×10^{20} g^{-1}. After gas adsorption at $P = 2 \times 10^2$ Pa, an increase in τ from 20 to 60 min resulted in a decrease in the intensity of the first peak by a factor of three. The dependence of the intensity of the peak at 370 K on τ and the pressure of the adsorbed gas reveals that this peak is likely due to the desorption of condensed ammonia from zeolite channels. On the other hand, the peak at 610 K, whose intensity does not change with τ and pressures of adsorbed NH_3, can be assigned to ammonia desorption from the Brönsted acid sites.

The peak at 350–370 K is also present in the desorption spectra upon ammonia adsorption at room temperature ($P = 2 \times 10^2$ Pa and τ = 20 min) on the preliminarily oxidized or reduced samples of 2.86% CuZSM-5 (Fig. 2a, spectra *1* and *2*). It is seen in Figs. 1 and 2a that, in the temperature range from 450 to 850 K, ammonia desorption from the oxidized sample is higher than those from the reduced sample and HZSM-5. In addition, the mass spectrometric data (Fig. 2b) show that the high-temperature peaks at 670 and 750 K that are present in the desorption spectrum are due to the conversion of ammonia to N_2 and H_2O. On the other hand, ammonia desorption spectra from the reduced samples CuZSM-5 and HZSM-5 are similar.

The difference in the ammonia desorption spectra from the oxidized and reduced zeolites CuZSM-5 (Fig. 2a, spectrum *3*) can be due to the formation of complexes by the interaction between several ammonia molecules and copper(II) cations. This assumption was studied in more detail.

2. Formation of Complexes in the Course of Ammonia Adsorption on the Cu^{2+} Cations in Zeolite Channels as Studied by ESR

A typical ESR spectrum from isolated copper cations in the channels of the oxidized 2.86% CuZSM-5 zeolite is presented in Fig. 3 (Spectrum *1*). Analysis of the spectrum according to [9] shows that copper cations exist in both the square-pyramidal ($g_{\parallel} = 2.33$, $A_{\parallel} = 170$ G) and square-planar ($g_{\parallel} = 2.29$, $A_{\parallel} = 180$ G) coordinations. The lines in the $g_{\perp}$ region of the ESR spectrum of the copper cations in these coordinations overlap significantly. This hampers the estimation of the $g_{\perp}$ and $A_{\perp}$ values from the spectrum. The spectra of copper cations in CuZSM-5 zeolites with various copper concentrations (0.15–2.86%) were described in more detail and the *g*- and *A* tensors were estimated in [7]. As follows from Fig. 3 (spectrum *1*), the amounts of copper cations in different coordinations are nearly the same because the ratio of the intensities of the corresponding lines in the ESR spectrum is ~1. The total concentration of the Cu^{2+} cations in these species is 8×10^{19} spin/g.

The ESR signal changes upon ammonia adsorption (Fig. 3, spectrum *2*), indicating interaction between copper cations and ammonia molecules. The hfs lines corresponding to the square-pyramidal coordination disappear, and only hfs lines of the copper cations in the square-planar coordination ($g_{\parallel} = 2.27$, $A_{\parallel} = 180$ G) remain. These data show that interaction between the ammonia molecules and isolated Cu^{2+} cations produces complexes in which copper cations are in the square-planar coordination. This interaction is rather strong so that the ESR spectrum does not change during evacuation of the sample for 1 h at room temperature.

Figure 3 (spectra *3*–*8*) shows that the ammonia–Cu^{2+} complexes decompose upon thermal evacuation of the sample with adsorbed ammonia at temperatures from 380 to 580 K for 10 min. Spectrum *8* recorded after this treatment at 580 K is identical to the initial spectrum *1* but is lower in intensity. Hence, upon the decomposition of complexes, a fraction of copper cations preserves initial coordinations and the other fraction is reduced by ammonia. Spectrum *8* does not change with a further increase in the temperature of treatment.

After reduction of 2.86% CuZSM-5 with hydrogen, a large fraction of Cu^{2+} cations transformed into Cu^{+} and Cu^{0} because the concentration of the isolated Cu^{2+} cations decreased from 8×10^{19} to 6×10^{18} g^{-1}. The ESR spectrum of the reduced sample is presented in Fig. 4 (spectrum *1*). In this case, copper cations in the sample are in the square-pyramidal coordination. The absence of the square-planar copper cations indicates that they are more efficiently reduced with hydrogen than the square-pyramidal copper cations. It is seen in Fig. 4 (spectrum *2*) that the interaction of Cu^{2+} with ammonia is accompanied by a change from the square-pyramidal to square-planar coordination of the copper cations. Also, 16 super-hyperfine structure (SHFS) lines in the $g_{\perp}$ region appear instead of four hfs lines. The SHFS lines are due to the interaction between electrons of Cu^{2+} and the ^{14}N nuclei of the NH_3 molecules. This fact also confirms the formation of the ammonia complexes.

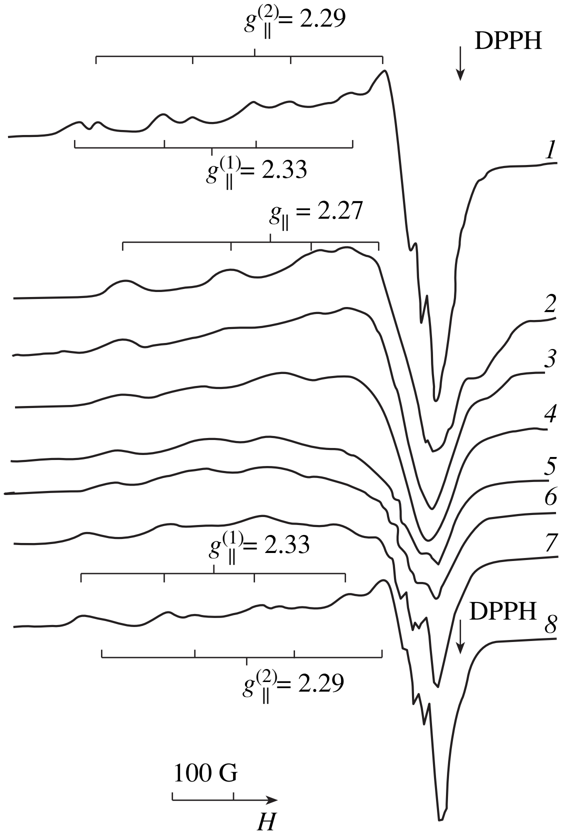

Fig. 3. ESR spectra of (*1*) preliminarily oxidized zeolite 2.86% CuZSM-5, (*2*) after admitting NH_3, (*3*) after evacuation at room temperature, and after heating and evacuation at (*4*) 380, (*5*) 430, (*6*) 480, (*7*) 480, and (*8*) 580 K for 10 min (*4*–*6*, *8*) and 20 min (*7*).

As can be seen in Figs. 3 and 2a (spectrum *3*), the temperature region of the variation in the ESR spectra (300–600 K) for the oxidized sample CuZSM-5 overlaps with that of the variation in the TPD spectra. The concentration of the NH_3 molecules desorbed from the copper(II) cations is 3×10^{20} g^{-1}, as follows from the TPD spectrum. Taking into account the Cu^{2+} concentration calculated from the ESR data, it is possible to estimate the average number of ligands in the complex of Cu^{2+} with ammonia. This value turns out to be ~4, and this agrees well with data from [9] in which the formation of the paramagnetic complexes $Cu^{2+}(NH_3)_4$ from the isolated copper cations was found.

3. Temperature-Programmed Nitromethane Desorption from HZSM-5 and 2.86% CuZSM-5 Zeolites

Desorption spectra observed upon nitromethane adsorption on HZSM-5 and 2.86% CuZSM-5 are presented in Fig. 5. As can be seen, an intense peak with a maximum at 360 K is present in spectra *1*–*3*, and this maximum is unaffected by the valence state of copper in the sample.

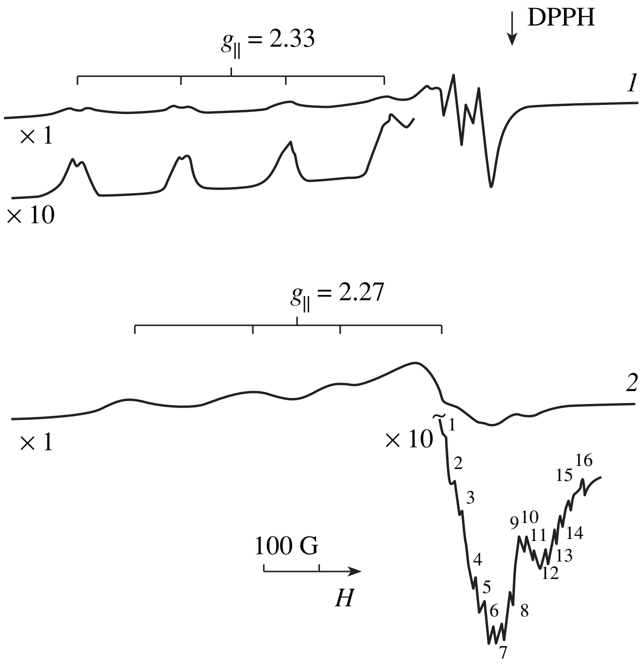

Fig. 4. ESR spectra of (*1*) preliminarily reduced zeolite 2.86% CuZSM-5 and (*2*) after NH_3 adsorption.

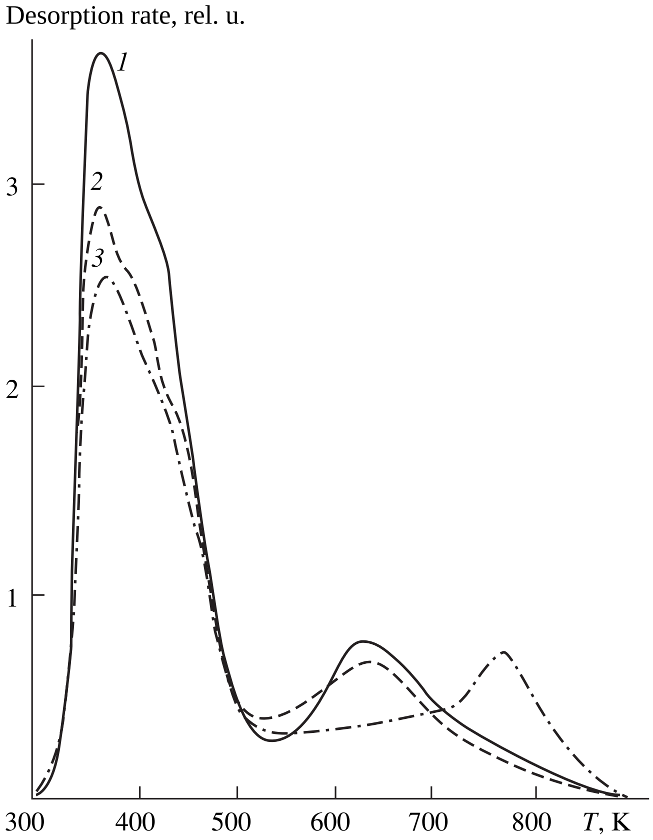

Fig. 5. TPD spectra after nitromethane adsorption on zeolites: (*1*) HZSM-5, (*2*) 2.86% CuZSM-5 preliminarily reduced with hydrogen and (*3*) oxidized with oxygen.

The mass spectroscopic data for HZSM-5 zeolite (Fig. 6a) show that nitromethane (15 and 30 amu) desorbs in the temperature range from 300 to 450 K; the products of nitromethane conversion—H_2O (18 amu), CO or N_2 (28 amu), and CO_2 (44 amu)—desorb in the range from 300 to 600 K, and ammonia (16, 17 amu) is desorbed at temperatures from 550 to 800 K. Similar mass spectra for the desorption of nitromethane and the products of its conversion were observed in the temperature range from 300 to 500 K for the oxidized and reduced 2.86% CuZSM-5 zeolites.

Figure 5 shows that the TPD spectra (spectra *1* and *2*) for HZSM-5 and reduced 2.86% CuZSM-5 virtually coincide. The peak with $T_{\max} = 630$ K is present in the spectra and corresponds to ammonia desorption (16 and 17 amu) (Fig. 6a). The desorption spectrum for the oxidized 2.86% CuZSM-5 zeolite has a complicated shape at temperatures above 500 K (Fig. 5, spectrum *3*). As follows from the mass spectroscopic data (Fig. 6b), NH_3, N_2, and H_2O desorb at $T_{\max} = 650$ and 750 K. The same products are present in the TPD spectrum for oxidized 2.86% CuZSM-5 upon ammonia adsorption (Fig. 2) at the same temperatures. This indicates that ammonia produced from nitromethane forms the same complexes as those formed upon ammonia adsorption from the gas phase.

4. Complex Formation in the Course of Nitromethane Adsorption on Cu^{2+} Cations Studied by ESR

Figure 7 presents the ESR spectra for the oxidized 2.86% CuZSM-5 before and after nitromethane adsorption at room temperature. Comparison of these spectra shows a variation in the parameters of the ESR spectra of the Cu^{2+} cations: the $g_{\parallel}$ values increase from 2.33 and 2.29 to 2.44 and 2.40 and the values of the hyperfine interaction constants $A_{\parallel}$ decrease from 170 and 180 G to 120 and 130 G, respectively. Based on the correlation of $g_{\parallel}$, and $A_{\parallel}$ with the coordination of the Cu^{2+} cations found in [9], one may suggest that an increase in $g_{\parallel}$ to 2.44 and 2.40 with a simultaneous decrease in $A_{\parallel}$ to 120 and 130 G indicates that Cu^{2+} cations, existing in zeolite channels both in the square-pyramidal and square-planar coordinations, appear in two different coordinations of distorted octahedra with $g_{\parallel} = 2.44$ and 2.40 because of interaction with nitromethane.

After desorption of nitromethane and the products of its conversion at 800 K, the concentration of Cu^{2+} cations decreased by 1/3 compared to the initial concentration because of the reduction of some fraction of copper cations with hydrocarbon fragments of nitromethane or with ammonia. The coordination of copper cations was found to be the same as in the oxidized samples before nitromethane adsorption.

DISCUSSION

1. Ammonia and Nitromethane Complexes with Brønsted Acid Sites and Cu^{2+} in Zeolites

Ammonia exists on HZSM-5 zeolite in the form of two species. The first species is associated with the desorption of condensed ammonia from zeolite channels at 370 K. The second one corresponds to ammonia desorption at $T = 610$ K from Brønsted acid sites, –Si–OH–Al–. In this case, the amount of desorbed ammonia, equal to $–1 \times 10^{20}$ g^{-1}, corresponds to the number of Brönsted acid sites in the zeolite that are accessible to gas adsorption [10].

According to [11], one can estimate the activation energy of ammonia desorption by the formula $E = 25RT_{max}$ provided that the second adsorption of the molecules inside zeolite channels does not occur. This estimate gives a value of ~127 kJ/mol for E for T_{max} = 610 K, and this value agrees with a bond energy of ~120 kJ/mol calculated for NH_4^+ cation. This cation was assumed to be adsorbed on two or three negatively charged oxygen atoms located around aluminum atom [12]. Despite approximations used in estimating the activation energy of desorption and bond energy, these values are comparable with the heat of ammonia adsorption on HZSM-5, which is equal to ~150 kJ/mol [10].

H^+ cations (1×10^{20} g^{-1}) in oxidized 2.86% CuZSM-5 zeolite are substituted for the $Cu^{2+}OH^-$ groups (8×10^{19} g^{-1}). Upon ammonia adsorption, copper cations are in the square-planar coordination (Fig. 3). The appearance of SHFS in the ESR spectrum (Fig. 4, spectrum *2*) upon ammonia adsorption on 2.86% CuZSM-5 preliminarily reduced with hydrogen provides evidence that ammonia molecules enter the ligand environment of copper cations. These data agree with those reported in [13], which show that the square-planar $Cu^{2+}(NH_3)_4$ complex is formed in the cages of the CuZSM-5 zeolite. The existence of the $Cu^{2+}(NH_3)_4$ complex was confirmed by calculations. It was shown in [14] that the ammonia molecules with the diameter $d \approx 4$ Å can form a copper complex with the coordination number of at most 4 in the cage of ZSM-5 with the linear size $L = 9$ Å.

Thus, one can assume that the interaction between ammonia molecules and copper cation results in the motion of the cation into a zeolite cage and the formation of the $Cu^{2+}(NH_3)_4$ complex.

Notably, at a high concentration of copper cations in zeolite (8×10^{19} g^{-1}), the ESR spectrum of $Cu^{2+}(NH_3)_4$ (Fig. 3) does not contain the SHFS lines. However, they are observed in the spectrum of the sample with a low concentration of copper cations (6×10^{18} g^{-1}) (Fig. 4). The absence of the lines from the ESR spectrum at high concentrations of supported copper can be due to dipole–dipole interaction between paramagnetic copper complexes, which results in the broadening of lines in the spectrum.

According to ESR data, the $Cu^{2+}(NH_3)_4$ complexes can be found in the temperature range from 300 to 500 K. According to TPD data, in the temperature range from 400 to 600 K, ammonia desorption from the oxidized zeolite 2.86% CuZSM-5 (Figs. 1 and 2) is higher than that from the reduced sample or zeolite HZSM-5. This difference in the TPD spectra is due to the decomposition of $Cu^{2+}(NH_3)_4$ complexes. This suggestion was confirmed quantitatively.

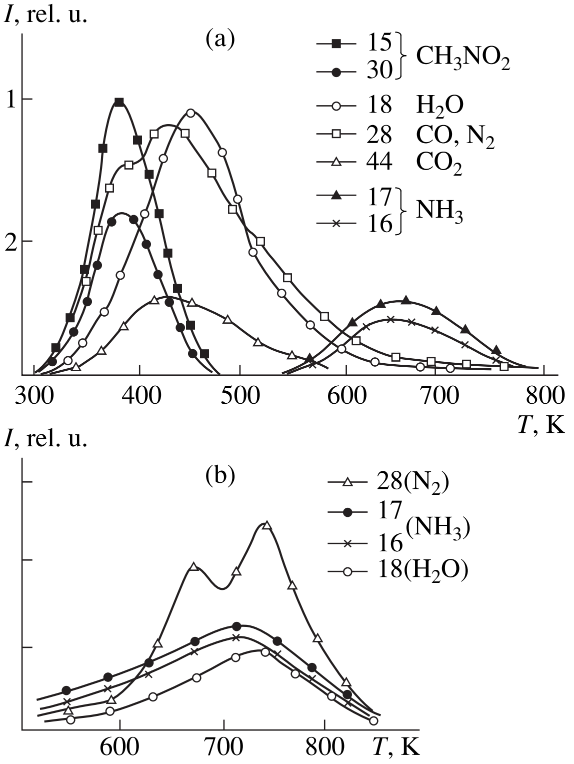

Fig. 6. Intensity (*I*) of lines of the mass spectrum during TPD after nitromethane adsorption on (a) zeolite HZSM-5 and (b) 2.86% CuZSM-5 oxidized with O_2.

The ammonia desorption spectra for the HZSM-5 and preliminarily reduced 2.86% CuZSM-5 are close (Figs. 1 and 2). As was shown earlier [15], the Cu^{2+} cations are transformed to Cu^+ and Cu^0 and the Brönsted acid sites of a zeolite are restored upon reduction of the copper-containing sample with hydrogen. Then, one can assume that in the preliminarily reduced copper-containing sample, ammonia mainly desorbs from the Brönsted acid sites of a zeolite and desorption from the Cu^+ and Cu^0 cations is negligible. Ammonia desorption from Cu^{2+} cations that are present in the reduced sample does not contribute substantially because of their low concentration. For this reason, desorption spectra recorded after nitromethane adsorption on the above samples coincide (Fig. 5).

Adsorption complexes, which are stronger than $Cu^{2+}(NH_3)_4$, are also formed upon ammonia adsorption on the oxidized 2.86% CuZSM-5 zeolite. They decompose at 650–750 K with the desorption of NH_3, H_2O,

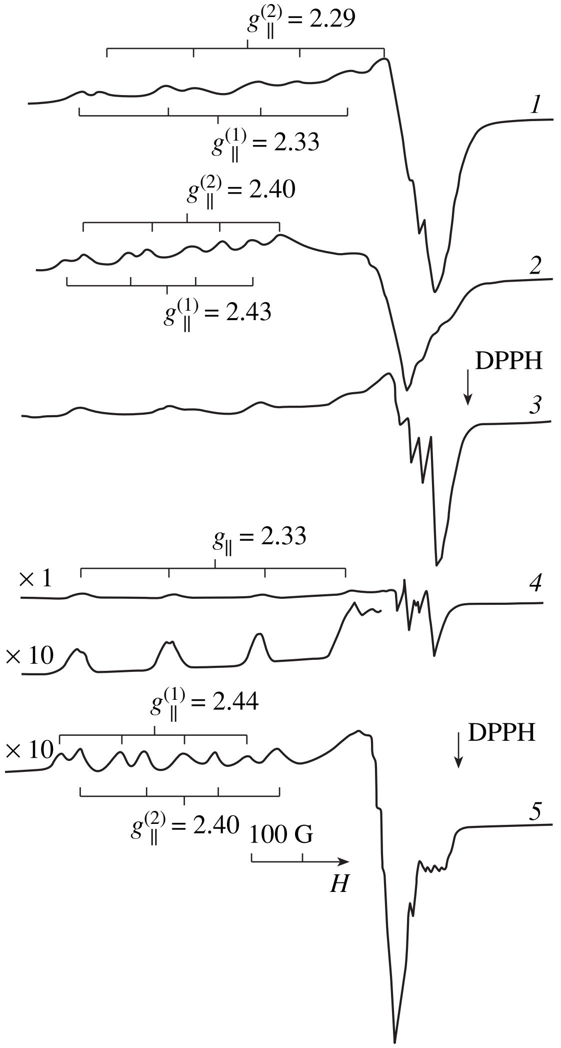

Fig. 7. The ESR spectra of (*1*) preliminarily oxidized zeolite 2.86% CuZSM-5, (*2*) after nitromethane adsorption, (*3*) after nitromethane desorption at 850 K and (*4*) preliminarily reduced zeolite 2.86% CuZSM-5, (*5*) after nitromethane adsorption.

and N_2. These complexes are formed on copper(II) cations because they are not found on the HZSM-5 and reduced 2.86% CuZSM-5. In the oxidized 2.86% CuZSM-5 zeolite, copper exists in various species. The concentration of the isolated Cu^{2+} cations (8×10^{19} g^{-1}) is ~50% of the total amount of supported copper. The rest of the copper(II) is present in zeolite as the $Cu^{2+}O^{-}$, $Cu^{2+}O^{2-}Cu^{2+}$ compounds and CuO clusters [7, 16–18]. These compounds contain an extra-framework oxygen, which participates in hydrocarbon oxidation [17]. These compounds were assumed to be active in the decomposition of NO to N_2 and oxygen [16]. We suggest that hydrogen formed upon deprotonization of NH_3 transforms into H_2O via the interaction with both an extra-framework oxygen and hydroxyls of the $Cu^{2+}OH^{-}$ sites. However, additional studies are necessary to conclude on the nature of the site of the ammonia adsorption and conversion.

In the course of nitromethane adsorption, the coordination of Cu^{2+} cations changes from square-pyramidal and square-planar to octahedral. It is barely possible that the octahedral complex consisting of a copper cation and nitromethane molecules will be formed in the zeolite cage since the size of this complex would be larger than the cage size because of the large size of the nitromethane molecule ($d \approx 5$ Å). In this case, one or two nitromethane molecules acting as ligands probably complete a pyramid and a square to an octahedron. Note that the $Cu^{2+}(NH_3)_4$ complex is not formed upon the decomposition of the octahedral copper complexes at 350–500 K. This can either be due to a deficit of ammonia molecules formed upon the decomposition of octahedral copper complexes with nitromethane or fast nitromethane conversion to other products.

2. Nitromethane Conversion to Ammonia over Zeolites

TPD data and mass spectroscopic analysis (Figs. 2, 5, and 6) show that ammonia is formed from nitromethane on both Brønsted acid sites and copper(II) cations. According to previously reported data [2–5, 19], nitromethane conversion into NH_3 over catalysts with various acid–base properties proceeds via an intermediate HNCO complex. We suggest that upon nitromethane adsorption on the HZSM-5 and 2.86% CuZSM-5 catalysts, ammonia, which desorbs from the Brönsted acid sites at 630 K and copper(II) at 750 K, is the product of such a conversion. Since the main features of the desorption of ammonia and the products of its conversion on CuZSM-5 upon nitromethane adsorption are the same as those upon NH_3 adsorption, it is obvious that ammonia is formed from nitromethane on the catalysts at temperatures lower than that of ammonia desorption and is stabilized on both the Brönsted acid sites and copper(II) cations. The desorption of other products of the nitromethane conversion, such as H_2O, CO, N_2, and CO_2, was observed at 350–450 K (see Fig. 6). Ammonia is likely formed from nitromethane at these temperatures.

The authors of [3] assume that the HNCO complex is a key intermediate in NO_x reduction by hydrocarbons over CuZSM-5 because its reactions with NO, NO_2, and O_2 result in nitrogen formation. If nitromethane corresponds to the initial nitrogen-containing organic compound and transforms into ammonia through such a complex, then this conversion should be completed at 450 K. Hence, only ammonia will be present on the catalysts surface at temperatures corresponding to NO_x reduction (600–800 K). Ammonia also reduces NO_x to N_2 [2]. Therefore, not only isocyanate complexes but also ammonia can participate in the formation of nitrogen from NO_x. This confirms a conclusion that the reduction of NO_x by hydrocarbons in excess oxygen over MZSM-5 zeolites (M = Co, H, Fe, and Cu) can proceed via a few final stages of the nitrogen formation from NO_x [20].

Our experiments showed that copper-containing zeolites are more active in NO_x reduction as compared to HZSM-5. We suggest that this difference can be due to the participation of strong ammonia complexes with copper(II) found in this study. The concentration of ammonia in the form of a complex with copper(II) in the CuZSM-5 catalyst is high at the reaction temperature (773 K) due to the decomposition of nitroxyl–hydrocarbon compounds. On the other hand, according to the data reported previously, ammonia is an excellent reducing agent for NO_x. The final conclusion on the reason for a difference in the activity of CuZSM-5 and HZSM-5 can be drawn only after a more detailed study of the nature of intermediates in this process.

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