Decomposition of N_2O on Cu/ZSM-5 Catalysts Obtained from Copper Complexes of Various Structures

R. A. SHUTILOV, V. YU. GAVRILOV

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

E-mail: gavrilov@catalysis.ru

Abstract

The use of copper oxide complexes (CC) of various structures: CC-I (copper tetrammine complex with the ground state of copper ions ($d_{x^2} - d_{y^2}$), characterized by a weak exchange magnetic interaction in the EPR spectra) and CC-III (Cu^{2+} ions with the ground state ($d_{x^2} - d_{y^2}$), with the strong exchange magnetic interaction) in the synthesis of Cu/ZSM-5 catalysts allowed us to study the effect of their structure on the physicochemical and catalytic properties in the decomposition of nitrogen (I) oxide (N_2O). It was demonstrated by means of H_2-TPR and IR spectroscopy of adsorbed CO that the nature of the reduction of Cu/ZSM-5 catalysts is determined by the state of copper in the catalyst. It was established that the highest catalytic activity is observed for the catalysts prepared using CC-III. Extraframework CuO-like clusters stabilized on the outer surface of zeolite crystallites prepared using CC-III are the most effective centres for the decomposition of nitrous oxide, and the activity of catalysts increases with an increase in copper content.

Keywords: copper oxide complexes, Cu/ZSM-5 catalysts, N_2O decomposition

INTRODUCTION

Copper-containing zeolite catalysts are relevant for solving urgent ecological problems connected with neutralization of greenhouse gas emissions ($DeNO_x$) – NO and N_2O destroying the ozone layer in the upper atmospheric layers. Anthropogenic sources of N_2O include the production of nitric acid and adipic acid used to manufacture nylon [1–4]. The development of the works aimed at solving ecological problems is also promoted by permanent toughening of Russian and international legislation in this area. Neutralization of N_2O emission may be carried out with the help of copper-containing zeolite catalysts.

It is known that Cu/ZSM-5 along with Fe/ZSM-5 demonstrates high catalytic activity in the decomposition of N_2O [3–11]. In addition, Cu/ZSM-5 catalysts are also active in other reactions of $DeNO_x$ including NO decomposition [12–19], selective catalytic reduction of NO_x with hydrocarbons or NH_3 [3, 4, 19–24]. Due to the catalytic properties of Cu/ZSM-5 catalysts, they are under intense investigation.

The major problem which is under study at present is the revelation of the nature, distribution of various kinds of copper in zeolite, their oxidation-reduction behaviour and analysis of interconnections between the structure and activity in a definite reaction of $DeNO_x$. In Cu/ZSM-5 catalysts synthesized by means of ion exchange with the aqueous solutions of different copper salts (acetate, nitrate, sulphate or chloride) [20, 25, 26], isolated Cu^{2+} ions were detected in the structural cation centres, and some types of extra-framework dinuclear and polynuclear complexes of copper ions [3, 4, 15, 25–30]. Tetra-, penta- or hexacoordinated clusters of Cu^{2+} ions may be arranged on channel walls but their positions do not differ from each other

substantially from the viewpoint of interaction energy [3, 31].

It was demonstrated in [23, 27] that polynuclear copper complexes $[Cu_2(\mu\text{-}O)_2]^{2+}$ with the Cu−Cu distance equal to 2.9 Å in the Cu/ZSM-5 catalysts are most active in N$_2$O decomposition. The high activity of the catalysts with short Cu−Cu distances is explained by the easy oxygen migration because two O atoms are included in the same dinuclear centre, which promotes their transformation into gaseous O$_2$. With an increase in the distance between copper centres, oxygen migration becomes hindered. So, the difference in oxygen migration explains the observed sequence of activity in N$_2$O decomposition: dinuclear oxo complexes of copper ions Cu^{2+} > polynuclear oxo complexes of copper ions Cu^{2+} > isolated Cu^{2+} ions [28, 32−34].

Copper particles may be also formed in the catalysts on the outer surface of zeolite crystals. Investigation of Cu/ZSM-5 catalysts by means of X-ray photoelectron spectroscopy (XPS) [35, 36] revealed the formation of coarse aggregated copper oxide particles on the outer surface of zeolite crystals in the catalysts obtained by means of impregnation, and their absence in the catalysts obtained by means of ion exchange. However, there is no consensus of opinion concerning the activity of CuO-like particles in the reactions of DeNO$_x$ [25, 35−38].

The method of synthesis (including precursor compounds) is the key parameter determining the nature, concentration and distribution of active copper species in the structure of zeolite Cu/ZSM-5 and their efficiency in the catalytic reaction. Nevertheless, no unambiguous correlation has been revealed between the method of Cu/ZSM-5 synthesis, the distribution of active copper species and the catalytic properties in the reactions of DeNO$_x$. For the purpose of improving the catalytic properties of Cu/ZSM-5, sequential investigation and optimization of the major stages of catalyst formation involving different copper-containing precursors are promising.

The possibility to govern the size, structure and positions of multinuclear copper species in Cu/ZSM-5 catalysts obtained by ion exchange with the aqueous ammonia solution of copper nitrate ammonia by varying the structure of the initial copper complex (CC) was demonstrated previously [39, 40]. The structure of the complex and the electronic state of copper in the aqueous ammonia solution of copper nitrate may be controlled by varying the NH$_4$OH/Cu ratio. The types of centres formed in Cu/ZSM-5 catalysts prepared using these precursors and their effect on the catalytic properties in the selective reduction of NO by propane were studied in [41, 42].

In the present work, we studied the effect of the state, position and oxidation-reduction properties of Cu/ZSM-5 catalysts obtained by means of ion exchange with copper-containing complexes of different structures on the catalytic properties in the decomposition of N$_2$O by means of diffuse reflectance spectroscopy (UV-vis DR), IR spectroscopy of adsorbed CO, temperature-programmed reduction with hydrogen (H$_2$-TPR) and temperature-programmed decomposition (TPD) of N$_2$O.

EXPERIMENTAL

To synthesize Cu/ZSM-5 catalysts, we used commercial zeolite HZSM-5 (NPCC, Russia) with Si/Al = 17 and crystallinity degree 95 %. The content of Fe^{3+} and Na$^+$ admixtures in the zeolite was 0.09 and 0.05 mass %, respectively. Before catalyst preparation, the zeolite was annealed in the air at 500 °C for 6 h. The Cu/ZSM-5 catalysts were synthesized by means of ion exchange [39]. Initial solutions were prepared by dissolving Cu(NO$_3$)$_2$ · 3H$_2$O (Aldrich, USA) in the aqueous solution of ammonia of the required concentration. Copper concentration was 10 g/L in all cases, while the ratio NH$_4$OH/Cu in solution was 23 (CC-I) and 3 (CC-III) [39, 40].

The chemical composition of initial solutions and the obtained catalysts was analyzed by means of atomic emission spectrometry with inductively coupled plasma with the help of an Optima 4300 DV spectrometer (PerkinElmer, USA) with the accuracy of 0.05−0.1 mass % following the standard procedure.

Diffuse reflectance (UV-vis DR) spectra of the catalysts were recorded using UV 2501 PC and UV 3101 PC spectrophotometers (Shimadzu, Japan) equipped with the attachment for diffuse reflectance ISR 250A within the ranges 11 000−54 000 cm^{-1} and 6000−12 000 cm^{-1} with respect to BaSO$_4$ as a reference. The measured spectra were transformed into Kubelka−Munk function $F(R)$ calculated as $F(R) = (1 - R)^2/2R$, where R is experimentally measured reflection index.

Oxidation-reduction characteristics of the samples were studied with the help of H$_2$-TPR. The reduction of H$_2$ samples was carried out in a flow reactor connected with the thermal conductivity detector.

The IR spectra of adsorbed CO were recorded with a Shimadzu 8300 spectrometer (Japan) with a resolution of 4 cm^{-1}. Each spectrum was scanned 100 times. The accuracy of concentration measurement was ±15 %. Spectrum deconvolution was carried out with the help of Origin software with the traditional assumption concerning the Gaussian shape of the spectra.

The activity of the catalysts in the decomposition of N_2O was tested in the steady and temperature-programmed modes in a flow quartz reactor with the static bed. Analysis of reaction products was performed by means of gas chromatography with the thermal conductivity detectors. The catalytic activity was evaluated from the dependence of N_2O conversion on the reaction temperature. A comparison of the activities of different catalysts was carried out over the temperature (T50) at which the 50 % conversion of N_2O is achieved.

Temperature-programmed decomposition of N_2O was carried out in a vacuum static set-up equipped with the RGA 200 mass spectrometer (Stanford Research Systems, USA) for the analysis of the gas phase [43].

RESULTS AND DISCUSSION

The forms of Cu^{2+} ion stabilization in concentrated aqueous ammonia solutions of copper nitrate within a broad range of ammonium ion concentrations were investigated previously [41, 42]. It was discovered by means of electron paramagnetic resonance (EPR) that the concentration of ammonia in the solution determines the type of orbital ordering of Cu^{2+} ions in the formed CC. In all cases, Cu^{2+} ordering is due to the presence of bridging OH groups in the axial and equatorial positions of $[Cu(NH_3)_n(H_2O)_{6-n}]^{2+}$ complexes ($n < 6$). With the high ammonia concentration in solution, according to EPR data, a complex of copper tetrammine with the ground state of Cu^{2+} ions ($d_{x^2} - d_{y^2}$) with weak exchange interaction is formed (copper complex of the I type, CC-I) (Fig. 1, a). In a solution with the low concentration of ammonia [40−42], associates of Cu^{2+} ions with the ground state ($d_{x^2} - d_{y^2}$) with strong exchange interaction are formed. They contain hydroxyl groups in the equatorial plane and water molecules in the axial position (copper complex of the III type, CC-III) (see Fig. 1, b). It should be
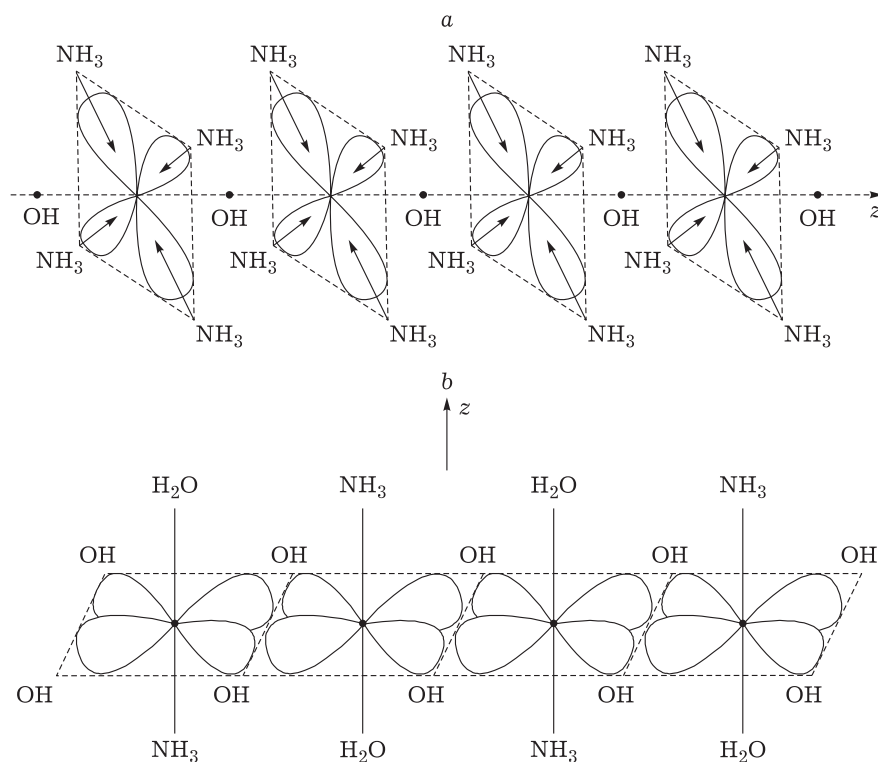

Fig. 1. Copper complexes CC-I (a) and CC-III (b).

stressed that similar complexes may also be obtained using aqueous ammonia solutions of copper chloride, sulphate and acetate [44, 45].

Figure 2 shows the UV-vis DR spectra of HZSM-5 and Cu/ZSM-5 samples prepared using CC-I and CC-III, after annealing at 500 °C [39]. In the spectrum of HZSM-5, only an edge of fundamental absorption 34 500 cm⁻¹ is recorded, which is due to the presence of the forbidden gap in the zeolite, which is typical for dielectric oxide structures [46]. The spectra of Cu/ZSM-5 catalysts obtained using CC-I and CC-III contain 12 000–12 500 and 47 500–48 000 cm⁻¹ absorption bands in the visible region of the spectrum. Energies of these bands correspond to the band of $d-d$-transitions ($T_{2g} - E_g$) and the charge transfer band (CTB) ligand → metal (L → Me) of isolated Cu^{2+} ions in the distorted octahedral surroundings with weak tetragonal distortions [47]. Besides, an additional absorption band at 35 000 cm⁻¹ is recorded in the UV region of UV-vis DR spectra for Cu/ZSM-5 prepared using CC-I, and for the catalyst prepared using CC-III, absorption bands are observed in the regions of 35 000 and 38 000 cm⁻¹. The energies of these bands correspond to CTB (O → Cu^{2+}) in the associates of copper ions with weak exchange interaction. For the sample containing 3.25 mass % Cu, obtained using CC-III, broadened UV-vis DR absorption edge in the low-frequency region may be the evidence of the presence of O → Cu^{2+} CTB in the region of 26 000–32 000 cm⁻¹. According to [47], this may be connected with the presence of copper ion clusters in the flat square oxygen coordination with strong exchange interaction Cu–O–Cu. The appearance of additional CTB O → Cu^{2+} may be the evidence of the formation of oxide clusters of Cu^{2+} ions with stronger covalence of the Cu–O bonds in comparison with that in the associates of copper ions characterized by O → Cu^{2+} CTB 35 000 cm⁻¹ [47]. Isolated Cu^{2+} ions are stabilized in the positions of cation exchange in the channels of ZSM-5 and were observed by the authors of [3, 4, 20, 25, 39].
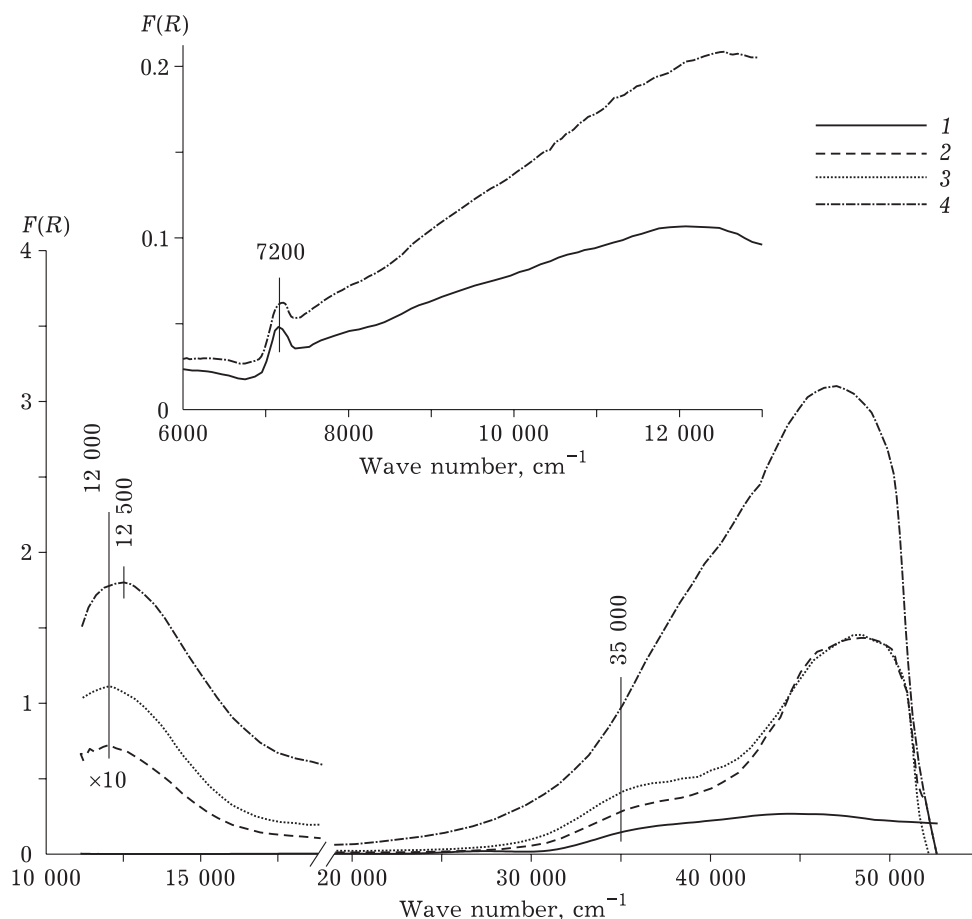

Fig. 2. UV-vis DR spectra of the samples of zeolite ZSM-5 (*1*) and catalysts 1.05 mass % Cu/ZSM-5 (*2*), 1.5 mass % Cu/ZSM-5 (*3*) obtained using CC-I, and the sample 3.25 mass % Cu/ZSM-5 obtained using CC-III (*4*). UV-vis DR spectra within the range 6000–12 000 cm⁻¹ [39] are shown in the insert.

TABLE 1

States and concentration of copper ions in Cu/ZSM-5 catalysts obtained by means of ion exchange using CC-I and CC-III, according to the data of IR spectroscopy of adsorbed CO [39]

Catalyst composition	Concentration of copper ions, $\mu mol/g$				
	ν, cm^{-1}			Cu_1*	Cu_2**
	2138	2157	2192		
1.72 mass % Cu/ZSM-5, CC-I	35	95	129	259	269
3.25 mass % Cu/ZSM-5, CC-III	53	107	140	300	508

 * From the data of IR spectroscopy of adsorbed CO.
 ** From the data of chemical analysis.

The UV-vis DR spectra within the range $6000-12\,000$ cm^{-1} are shown in the insert in Fig. 2. These spectra demonstrate a weak absorption band at 7200 cm^{-1}, which appears as a result of $d-d$-transitions ($E_g - T_{2g}$) of Cu^{2+} ions in the distorted tetrahedral oxygen environment. This band is likely to be connected with the presence of the traces of copper aluminate [47].

The IR spectra of adsorbed CO on the catalysts prepared using CC-I and CC-III contain three absorption bands with wavenumbers $\nu = 2138$, 2157 and 2192 cm^{-1}, which correspond to the vibrations of C–O bonds in different CC (Table 1) [39]. According to [48–53], the absorption band ($\nu = 2157$ cm^{-1}) is due to the stretching vibrations in the monocarbonyl (Cu^+–CO) complex. The band ($\nu = 2138$ cm^{-1}) is characteristic of monocarbonyl complexes (Cu^+–CO and Cu^{2+}–CO) in two-dimensional CuO clusters. The band ($\nu = 2192$ cm^{-1}) corresponds to dicarbonyl (Cu^+–$(CO)_2$ and Cu^{2+}–$(CO)_2$) complexes of Cu^{2+} ions within oxide CuO clusters. In both catalysts, the band at $\nu = 2192$ cm^{-1} dominates in the spectra. However, the highest concentration of this type of complexes is observed in the Cu/ZSM-5 catalyst obtained using CC-III.

With an increase in copper content, the fraction of each of the observed states increases. It should be stressed that in the catalysts obtained using CC-I and CC-III the total copper content is 1.72 and 3.25 mass %, respectively. However, we did not detect a proportional increase in the concentrations of all the observed states of copper with an increase in total copper content. It is interesting that the total concentration of copper measured by means of IR spectroscopy in the sample prepared using CC-I is 97 % of the concentration determined by means of chemical analysis. This may be the evidence of the small

size of the formed clusters of copper ions. In the sample prepared using CC-III, only about 59 % of the total amount of copper is recorded by means of IR spectroscopy. This may be the evidence of the formation of larger clusters in the case of the use of CC-III, so that only a part of copper ions is available for CO chemisorption.

A rough estimation of the change in the concentrations of all types of hydroxyl groups in the initial zeolite, carried out previously [40], with the amount of copper adsorbed by the zeolite after ion exchange with the solutions containing CC-I and CC-III, showed that copper content in the zeolite is much higher than the value corresponding to the stoichiometry of exchange ($2H^+$ per one Cu^{2+} ion). This may be the evidence that copper is localized in the zeolite not only as isolated Cu^{2+} ions but also in the form of associates.

According to the data reported in [40] on the distribution of copper within the volume of pores in Cu/ZSM-5 obtained on the basis of H_2 and N_2 adsorption at 77 K, the arrangement of copper particles on the surface of zeolite crystallites causes partial blocking of the volume of microporous channels for N_2 molecules bur has no effect on the availability of channels for H_2 molecules. The degree of blocking depends on the method of catalyst synthesis and is determined by the size and concentration of copper clusters located at the outer surface of the zeolite (in the volume of mesopores). The smallest clusters are formed during catalyst preparation by means of ion exchange with the solution of CC-I, larger clusters are formed in the case of CC-III. It is clear that the differences in the sizes of copper clusters provide different degrees of copper involvement in the catalytic reaction.

Figure 3 shows the results of H_2-TPR for the catalysts prepared using CC-I and CC-III [39]. The TPR curve for the Cu/ZSM-5 catalyst obtained using CC-I contains two clearly pronounced peaks at a temperature of 223 and 502 °C, and an extended shoulder with the maximum at 270 °C. The low-temperature peak at 223 °C and the shoulder at 270 °C correspond to the reduction of Cu^{2+} ions to Cu^+. The presence of a shoulder is the evidence of the presence of at least two types of Cu^{2+} ions differing from each other by the strength of the Cu–O bond. The peak on the TPR curve at a temperature of 502 °C corresponds to the reduction of Cu^+ ions to Cu^0 [35] in associates.

The catalyst obtained using CC-III demonstrates a clear splitting of the peak of low-temperature reduction into two peaks (at 223 and
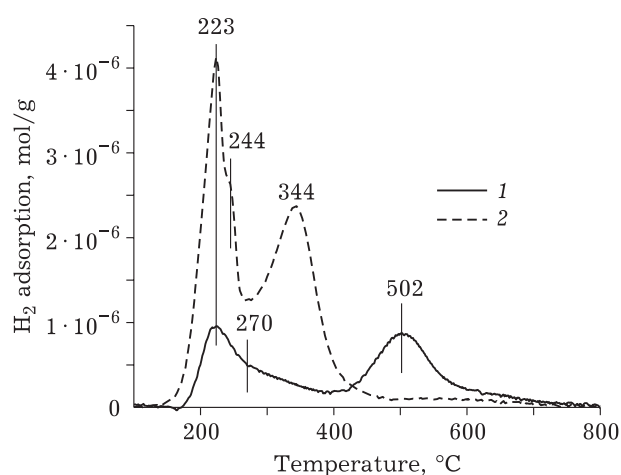
Fig. 3. TPR curves for Cu/ZSM-5 catalysts containing 1.4 mass % Cu (CC-I) (*1*)
and 3.25 mass % Cu (CC-III) (*2*) [39].

244 °C and a high-temperature peak at 344 °C. The additional peak at 244 °C points to the presence of at least two types of Cu^{2+} ions with different strength of the Cu−O bond. According to [15, 25, 30, 54, 55], low-temperature peaks at T ≈ 220 °C relate to the simultaneous processes of the reduction of isolated Cu^{2+} ions to Cu$^+$ and the reduction of Cu^{2+} ions in disperse CuO-like clusters to Cu^0. The high-temperature peaks correspond to the reduction of Cu$^+$ ions to the Cu^0 state.

One can see that the differences in the reducibility of the studied catalysts at the Cu$^+$−Cu^0 stage is substantially higher than at the Cu^{2+}−Cu$^+$ stage. This may point to the stronger binding of copper ions with the framework oxygen of the zeolite structure. The maximum of the peak of high-temperature reduction on the H$_2$-TPR curve for the catalyst prepared with CC-III decreases in comparison with the catalyst prepared with CC-I. Easy reducibility of the catalyst obtained using CC-III may be due to the high concentration of CuO-like clusters dispersed in the zeolite with the weak metal-oxygen bond, and the reduction of Cu$^+$ ions to Cu^0.

The catalytic properties of the obtained catalysts measured under steady conditions are presented in Fig. 4 and in Table 2 [56]. One can see (see Fig. 4) that, with the same copper concentration, the catalysts prepared using CC-III are more active than the catalysts prepared using CC-I. For instance, for the catalyst containing 1 mass % Cu and prepared using CC-I, 50 % conversion of N$_2$O is not achieved up to 500 °C, while the T_{50} is

achieved at 466 °C with the catalyst containing 1 mass % Cu and prepared using CC-III. The highest activity is characteristic of the catalyst containing 3.25 mass % Cu/ZSM-5 and prepared using CC-III, on which T_{50} is achieved at 368 °C, and T_{100} at 400 °C.

The experimental data on the adsorption and TPD of N$_2$O on the catalysts obtained using CC-I and CC-III are presented in Fig. 5 [56]. A plot of the TPD of TPD of N$_2$O on the catalyst containing 3.25 mass % Cu/ZSM-5 and obtained using CC-III is shown in Fig. 5, *a*. One can see that the injection of N$_2$O into the reactor at a temperature of 30 °C leads to the complete adsorption of N$_2$O. After the establishment of adsorption equilibrium and subsequent temperature rise from 30 to 300 °C, partial desorption and decomposition of N$_2$O is observed, with the release of molecular nitrogen alone into the gas phase, while oxygen is stabilized on the surface. The evolution of oxygen into the gas phase occurs only at a temperature above 320 °C, therefore, under these conditions the decomposition of N$_2$O proceeds with the evolution of stoichiometric amounts of N$_2$ and O$_2$ into the gas phase.

A TPD plot on the catalyst with the Cu content 1.72 mass % obtained using CC-I is shown in Fig. 5, *b*. In this case, when N$_2$O enters the reactor, only its partial adsorption occurs, and temperature rise leads to almost complete desorption of N$_2$O. The pressure of N$_2$O recovers its initial value, which remains constant at a temperature below 320 °C, then slowly decreases with further
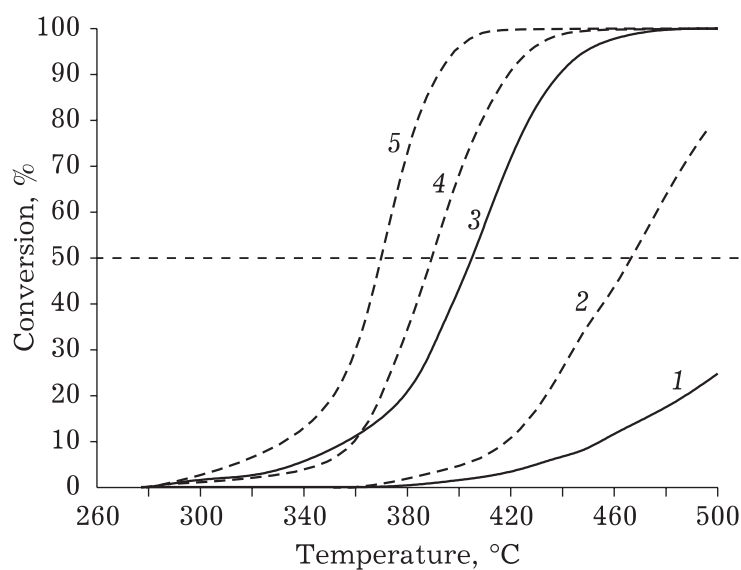
Fig. 4. Dependence of N_2O conversion on temperature for Cu/ZSM-5 catalysts containing 1 mass % Cu (*1, 2*), 2 mass % Cu (*3, 4*), 3.25 mass % Cu (*5*), obtained using CC-I (*1, 2*) and CC-III (*3–5*) [56].
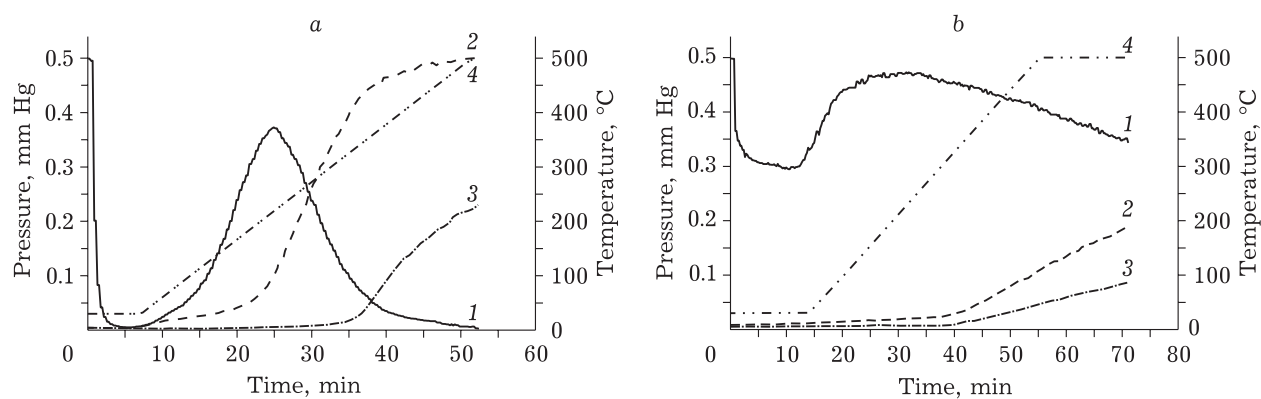
Fig. 5. TPD curves for N_2O on the catalysts 3.25 mass % Cu/ZSM-5 prepared using CC-III (*a*), and 1.72 mass % Cu/ZSM-5 prepared using CC-I (*b*). The curves of N_2O pressure change (*1*), N_2 (*2*), O_2 (*3*), temperature change (*4*) [56].

TABLE 2

Catalytic properties of catalysts [56]

Catalyst No.	Type of Cu complex	Cu content in Cu/ZSM-5 catalysts, mass %	Temperature at which 50 % conversion of N_2O (T_{50}) is achieved, °C
1	CC-I	1.0	–
2	CC-III	1.0	466
3	CC-I	1.72	404
4	CC-III	1.74	387
5	CC-III	3.25	368

temperature rise. At a temperature above 320 °C, stoichiometric decomposition of N_2O with the formation of small amounts of N_2 and O_2 starts.

CONCLUSION

Thus, copper compounds with different structures, CC-I and CC-III, used to prepare Cu/ZSM-5 catalysts by means of ion exchange, determine the concentration and the active state of copper during the decomposition of N_2O. The complexes of copper tetrammine with the ground electronic state $(d_{x^2} - d_{y^2})$, characterized by the weak exchange magnetic interaction (CC-I), and associates of Cu^{2+} ions with the ground electronic state $(d_{x^2} - d_{y^2})$ with hydroxyl groups in the equatorial plane and water molecules in the axial position, characterized by the strong exchange magnetic interaction (CC-III), may be obtained by the dissolution of copper nitrate in the aqueous solution of ammonia with the ratio $NH_4OH/Cu = 23$ and 3, respectively.

A substantially larger amount of copper is observed in the catalysts obtained using the ion exchange method with CC-III under equilibrium conditions in comparison with the catalysts prepared using CC-I. The activities of both catalysts increase with an increase in copper content. However, with close copper concentrations, the catalyst prepared using CC-III, is more active than that obtained using CC-I.

Extra-framework CuO-like clusters formed during the temperature treatment of Cu/ZSM-5 catalysts obtained using CC-III are more active in the decomposition of N_2O.

Acknowledgements

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