

The Stability of Monolith CuZSM-5 Catalysts for the Selective Reduction of Nitrogen Oxides with Hydrocarbons: I. Synthesis and Characterization of Bulk CuZSM-5 Catalysts

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Abstract—The effects of ion-exchange conditions (the pH, the copper concentration in solution, and the solution-to-zeolite volume ratio) and the Si/Al atomic ratio of HZSM-5 zeolite on the concentration and state of copper in bulk CuZSM-5 catalysts and on the catalytic activity in the selective reduction of NO with propane were studied. It was found that the concentration and state of copper in the catalysts essentially depend on the pH of the solution used for ion exchange and on the copper concentration in this solution. An increase in the solution-to-zeolite volume ratio has almost no effect on the above characteristics. Regardless of the Si/Al atomic ratio of zeolite and of the pH of solution, a maximum activity (NO conversion) of the resulting catalyst is attained even at an exchange level (Cu/Al) close to 100% (80–140%). The absolute value of this catalytic activity depends only on the reaction temperature and is equal to 22–31% at 300°C or 85–97% at 400–500°C. The above exchange level is maximally attainable at pH ~6 in the chosen range of copper acetate concentrations in solution (2–10 mg/ml accounted as CuO). An increase in the pH of ion exchange up to ~100% allows a wider variation in the exchange level and the state of copper in the zeolite with the same range of copper concentration in the solution. However, at Cu/Al \geq 100% (up to ~430%), the catalyst activity is independent of the exchange level. The state of copper in freshly prepared samples affects the stability of the catalysts in storage. In turn, the state of copper depends on ion-exchange conditions and the Cu/Al ratio.

INTRODUCTION

It is well known that copper-substituted zeolites, in particular, CuZSM-5, are active catalysts in the selective catalytic reduction of nitrogen oxides with hydrocarbons in a temperature range of 300–500°C. The most detailed data on the characterization and application of these catalysts were published [1–6]. Nevertheless, copper-substituted zeolites are not always efficient in practical use. This is primarily due to their low stability in the presence of water vapor, which is responsible for the reversible or irreversible deactivation of CuZSM-5 at temperatures lower than 500°C or equal to ~600°C, respectively [3, 5–7]. Moreover, the activity of copper-containing zeolite catalysts also decreases in the presence of poisons such as SO₂ [5]. Finally, in the practical use of these catalysts, for example, for purifying industrial gases of nitrogen oxides (only honeycomb catalysts should be used in this case to decrease the gas-dynamic resistance), a serious problem is to attain a sufficiently high mechanical strength of intricately shaped zeolite monoliths.

A route of the development of resistant and active monolith catalysts based on metal-substituted zeolites

consists of the use of high-strength monolith carriers (for example, blocks based on sintered ceramics with required shapes and superficial measures, as well as with required shapes and sizes of the channels) followed by supporting a catalytic zeolite layer as a washcoating. Data on the preparation and characterization of such catalysts were published in a few papers, in which the properties of Co- and Cu-substituted zeolites supported as washcoatings were discussed [8–10]. However, data on the possibility to control the activity of monolith catalysts of this type by varying preparation conditions, on their resistance to poisons and attrition, and on their stability in storage are almost absent from the literature.

This work, which consists of three parts, is devoted to the effects of the preparation conditions of monolith catalysts containing CuZSM-5 in a washcoating on the activity in selective NO reduction with propane, on the resistance to water vapor and SO₂ impurities, and on the stability in storage.

It is obvious that, first, conditions required for producing a bulk (unsupported) CuZSM-5 catalyst with optimum catalytic and other characteristics should be found to develop efficient monolith catalysts with an

Table 1. Main characteristics of initial HZSM-5 zeolite samples

Sample	S_{BET} , m ² /g	V_{Σ} , cm ³ /g	V_{μ} , cm ³ /g	Chemical composition, wt %							Si/Al, atom/atom
				Al	Si	K	Na	Mg	Ca	Fe	
I	380	0.239	0.095	0.69	50.4	0.03	0.08	0.02	0.05	0.50	73
II	380	0.255	0.125	1.11	37.7	0.02	0.03	0.03	0.05	0.55	34

active washcoating. That is, the effects of the properties of parent zeolite, the conditions of ion exchange, and the state of copper on the properties of this catalyst should be examined. The first part of this study is devoted to these problems.

EXPERIMENTAL

Two HZSM-5 zeolite samples different in the Si/Al atomic ratio, which were prepared on a pilot scale,¹ were used for preparing CuZSM-5 catalysts. Table 1 summarizes the main properties of these samples.

The specific surface areas (S_{BET}) of samples were determined by the thermal desorption of argon; the total pore volume (V_{Σ}) and the micropore volume (V_{μ}) were determined from nitrogen adsorption isotherms. The phase composition and the size of primary particles were determined from X-ray diffraction.²

The CuZSM-5 catalysts were prepared by ion exchange using copper acetate solutions (pH ~6) and an ammonia solution of copper acetate (pH ~10). The copper concentration (accounted as CuO) in these solutions and the solution-to-zeolite (S/Z) volume ratio were varied.

The copper contents of the samples were determined by chemical analysis. The exchange level in zeolite was expressed as the Cu/Al atomic ratio or as a percentage. In this case, analogous to [6, 11, 12], we believed that 100% exchange corresponded to an amount of introduced copper equal to half the atomic concentration of aluminum in the sample; that is, the exchange level is theoretically equal to 100% at Cu/Al = 0.5.

The structures of the parent zeolite samples and CuZSM-5 catalysts were studied by NMR spectroscopy. The state of copper in the catalysts was characterized by IR spectroscopy (using CO adsorption) and XPS.

The IR spectra were measured on a BOMEM MB 102 FTIR spectrometer. The catalysts were pressed as pellets 10–20 mg/cm² in thickness and placed in a special cell, which made it possible to perform both the

high-temperature treatment of samples and the low-temperature adsorption of gases. The samples were pre-treated in a vacuum at 10^{−3} torr and 450°C for 4 h to remove adsorbed compounds and water. The admission of CO was performed at $P_{\text{CO}} = 1.5$ torr. The spectra of adsorbed CO were measured at room temperature and at a temperature of liquid nitrogen (−196°C).

The XPS spectra were recorded on an ESCA-3 X-ray photoelectron spectrometer with the use of AlK_α radiation in accordance with the published procedure [13]. The C1s signal, which was taken equal to 284.8 eV, was used as reference.

The ²⁷Al NMR spectra were measured on a Bruker MSL-400 pulse Fourier spectrometer (magnetic field of 9.4 T) at 104.2 MHz with the use of a magic-angle spinning (MAS) probe. The pulse duration was 5 μs; the pulse-to-pulse delay was 0.5 s; the number of scans was 3200; and the sample spinning rate was 10.6 kHz. The chemical shifts of ²⁷Al were determined to within ±0.5 ppm with reference to [Al(H₂O)₆]³⁺ as an external standard.

The activity of the catalysts was characterized by NO conversion in the reaction of nitrogen oxide reduction with propane. The reaction was performed in a flow reactor at 300–600°C under the following conditions: catalyst volume of 4 cm³ and space velocity of 42000 h^{−1}. The composition of the initial gas mixture was as follows: NO ~ 300 ppm; C₃H₈ ~ 0.15 vol %; O₂ ~ 3.5 vol %; and balance N₂. The initial gas mixture and reaction products were analyzed on an ECOM-SG^{plus} gas analyzer with the sensitivities of 1 ppm for NO, NO₂, and CO; 0.01 vol % for C₃H₈; and 0.1 vol % for O₂.

RESULTS AND DISCUSSION

Table 1 indicates that HZSM-5 zeolite samples with different Si/Al atomic ratios are insignificantly different in impurity concentrations. The iron contents of the samples are reasonably high. To evaluate the role of impurity iron in the activity of the CuZSM-5 catalysts, the initial zeolite samples were tested in the reaction of NO reduction with propane. We found that NO conversion on HZSM-5 does not exceed 5–8% over the entire temperature range. Therefore, the contribution of impurity iron to the activity can be neglected.

The pore-structure parameters of the zeolite samples in use are similar to published values [14–16]. The

¹ We are grateful to I.E. Abros'kin for the provision of the samples.

² We are also grateful to V.B. Fenelonov for the study of the pore structure of zeolites and to V.A. Ushakov for the XPS study of zeolites.

X-ray diffraction patterns of both samples are identical, and they correspond to the structure of HZSM-5 published in [14]; the crystal sizes (coherent-scattering regions) are equal and amount to ~ 750 Å.

A comparison between the ^{27}Al NMR spectra of samples I and II exhibited a difference in the signal intensities of Al^{3+} in a tetrahedral coordination, which depend on the amount of aluminum cations in the zeolite structure. In both of the samples, Al^{3+} in an octahedral coordination was detected in trace amounts (~ 1 – 3%).

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The copper content and hence the exchange level remained almost unchanged in the test catalysts upon varying the S/Z volume ratio from 10/1 to 50/1 at different pH of solution. Therefore, all of the subsequent experiments were performed at $S/Z = 10/1$.

Table 2 summarizes the effects of the Si/Al atomic ratio, the concentration of copper in solution, and the pH of solution on the copper content and the exchange

level in the catalysts. As can be seen, the copper contents (exchange levels) of samples decreased with decreasing copper concentration in solution regardless of pH and the zeolite Si/Al atomic ratio. At similar concentrations of solutions, the copper contents of samples prepared at pH ~ 10 are higher than those in the samples prepared at pH ~ 6 regardless of the zeolite Si/Al atomic ratio. At pH ~ 10 , the copper content tends to increase with the zeolite Si/Al atomic ratio.

Table 2 also summarizes the results of testing the activity of the prepared catalysts. It follows from these data that, over the chosen ranges of the above ion-exchange parameters and the zeolite Si/Al atomic ratios, the samples exhibit no considerable difference in the activity. A maximum activity (NO conversion) of the test catalysts was attained even at an exchange level (Cu/Al) close to 100% (80–140%), and its absolute value depends only on the reaction temperature and is equal to 22–31 or 85–97% at 300 or 400–500°C, respectively. At pH ~ 6 , the above exchange level is maximally attainable in the chosen range of copper acetate concentrations in solution (2–10 mg/ml accounted as CuO). The results of this study are consistent with published data [17].

Table 2. Properties of bulk CuZSM-5 catalysts as functions of the conditions of ion exchange and of the zeolite Si/Al atomic ratio

Zeolite Si/Al atomic ratio	Cu concentration		Cu/Al, %	NO conversion, %, at temperatures, °C				
	in solution, mg/ml (accounted as CuO)	in catalyst, wt %		300	350	400	450	500
Ion exchange from copper acetate (pH ~6)								
73	10.0	1.16	140	22	70	91	93	91
	5.0	1.00	118	26	63	88	94	93
	2.0	0.90	110	24	69	87	90	90
34	10.0	1.26	96	25	70	85	92	92
	5.0	1.12	86	28	71	94	97	96
	2.0	1.07	80	24	71	94	97	96
Ion exchange from copper ammoniate (pH ~10)								
73	8.5	3.53	428	31	68	94	99	97
	8.0	2.94	356	30	71	89	89	88
	4.0	2.44	296	31	70	85	90	90
	2.0	1.50	182	26	69	88	90	89
	1.0	0.98	120	24	68	85	86	86
34	8.0	2.27	172	25	67	90	92	90
	4.0	1.93	146	30	77	92	93	91
	2.0	1.45	110	28	72	89	92	92

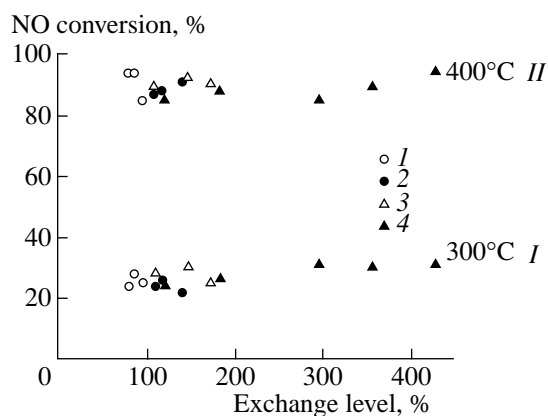


Fig. 1. NO conversion in the reduction reaction with propane at (I) 300 and (II) 400°C on CuZSM-5 catalysts with Si/Al = (1, 3) 34 and (2, 4) 73 as a function of ion-exchange level at pH (1, 2) ~6 and (3, 4) ~10.

An increase in the pH of ion exchange (ammonia solutions of copper acetate with pH ~10) makes it possible to vary the exchange level much more widely over the same range of copper concentrations in solution. However, at Cu/Al \geq 100% (up to ~430%), the activity of catalysts remained almost unchanged as compared with catalysts having Cu/Al ~100% (Table 2, Fig. 1). Thus, the use of copper acetate solutions with pH ~6 for ion exchange is preferable because these solutions are easier to use in terms of processing.

An excessive copper content (above 100% exchange level) of samples prepared at pH ~10 can be responsible for a decrease in the activity of these catalysts in long-term storage, as shown in Table 3. These results suggest that the state of copper, which is responsible for the nature and amount of active centers, is also changed upon varying ion-exchange conditions and the zeolite Si/Al atomic ratio in catalysts. Table 3 indicates that the activity of an aged catalyst was not restored after regeneration.

We used NMR and IR spectroscopy and XPS for studying the state of copper in catalysts depending on ion-exchange conditions and the duration of storage.

Table 3. Activity of a bulk CuZSM-5 catalyst (Si/Al = 73; 3.53 wt % Cu) in the reduction of NO with propane as a function of storage time

State of the catalyst	NO conversion, %, at temperatures, °C				
	350	400	450	500	550
Fresh, pH ~10	71	89	89	88	88
After 1.5 years	61	76	79	73	71
After regeneration	64	76	73	66	65

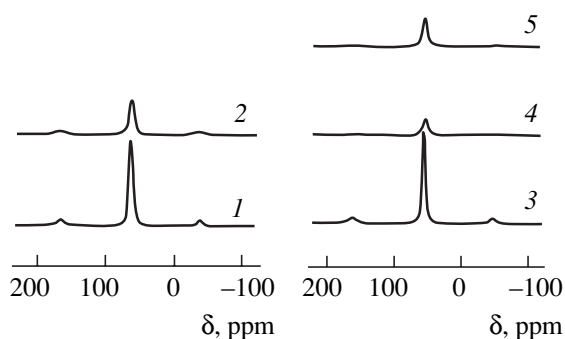


Fig. 2. ^{27}Al NMR spectra of HZSM-5 zeolites with Si/Al = (1) 34 and (3) 73 and of (2) 2.27% CuZSM-5 (Si/Al = 34) and (4) 3.53% CuZSM-5 (Si/Al = 73) catalysts prepared at pH ~10; (5) the spectrum of the 3.53% CuZSM-5 (Si/Al = 73) catalyst after long-term storage.

The Structure of Bulk Copper-Substituted Zeolites According to NMR Data

The introduction of copper into zeolites does not considerably affect the ^{27}Al NMR spectra: only the intensity of a signal due to Al^{3+} in a tetrahedral environment decreases as compared to that of the initial zeolite (Fig. 2). This is due to the paramagnetic broadening of an aluminum signal: a portion of Al^{3+} directly bound to Cu^{2+} compounds becomes “invisible” because of a considerable width of the signal. The higher the Cu/Al ratio in zeolite, the more considerable the decrease in the Al^{3+} signal intensity.

After the long-term storage of a catalyst containing 3.53% Cu on zeolite with Si/Al = 73 (Cu/Al = 2.14 or 428%), the ^{27}Al signal intensity in the NMR spectrum somewhat increased (Fig. 2). It is likely that an excess of copper over aluminum in this catalyst facilitates the formation of coarsely dispersed structures up to individual copper oxide in storage. In this case, the number of aluminum cations directly bound to bivalent copper decreases, and the signal due to ^{27}Al increases as compared to a fresh sample. This fact suggests that Cu^{2+} compounds unbound from Al^{3+} are formed in storage.

XPS Data

Table 4 summarizes the Cu/Si atomic ratios and the binding energies for copper cations in catalysts with Si/Al = 73 prepared at different pH values, as calculated from XPS data. It can be seen that in the catalyst prepared at pH ~10 the binding energy is higher by 1.7 eV and the Cu/Si ratio is higher by an order of magnitude than the corresponding values in the catalyst prepared at pH ~6.

Taking into account published data on the binding energy of copper cations in zeolites [18, 19] and the results given in Table 4, we can conclude that reduced copper species (Cu^+ and Cu^0 states) occur in the catalyst prepared at pH ~6. It is well known that the binding

energies of these species are lower than that of Cu^{2+} by ~ 1 to 2 eV. The reduced copper species can be formed in the course of ion exchange, or they can result from highly dispersed bivalent copper under exposure to an electron beam in the course of XPS measurements. At pH ~ 10 , surface Cu^{2+} cations are primarily formed as highly dispersed CuO. However, the occurrence of reduced copper species in this case also cannot be excluded based on an analysis of the shape of spectra.

At pH ~ 6 , the bulk and surface concentrations of copper (according to XPS data) are close to each other. This fact allowed us to conclude that in this case, the copper distribution is fairly homogeneous. This is consistent with published data that explain the high activity of copper-substituted zeolites prepared from copper acetate at pH ~ 6 . It was noted [19–21] that highly dispersed structures (clusters) based on Cu^{2+} are readily reduced by NO to Cu^+ cations under reaction conditions. These Cu^+ ions activate the process of selective NO reduction with hydrocarbons.

IR-Spectroscopic Data for Adsorbed CO^3

Below are known data on the adsorption of CO on copper-containing catalysts; these data were taken into account in an analysis of IR spectra.

At room temperature, CO is not adsorbed on bivalent copper cations. However, at reduced temperatures, the spectrum exhibits an absorption band at 2190 cm^{-1} , which was ascribed to CO complexes with Cu^{2+} cations [22, 23]. At room temperature, the spectrum of CuZSM-5 exhibits the only absorption band at $\sim 2157\text{ cm}^{-1}$ [24, 25], which corresponds to monocarbonyl complexes of CO with Cu^+ . An increase in the surface coverage with adsorbed CO as the temperature decreased resulted in a shift of this absorption band toward a low-frequency region to 2151 cm^{-1} and in the appearance of a new absorption band at 2177 cm^{-1} in the spectrum. These bands were attributed to the anti-symmetric and symmetric stretching vibrations of dicarbonyl Cu^+ complexes, respectively [24]. A low-frequency absorption band at 2110 cm^{-1} , which appears in reduced samples, is ascribed to CO adsorbed on Cu^0 or Cu^+ . A broad absorption band at 2137 cm^{-1} can be attributed to CO adsorbed on Cu^+ cations that are located on the surface of CuO crystallites by analogy with the $\text{CuO}/\text{Al}_2\text{O}_3$ system [22].

The IR spectra of CO on freshly prepared CuZSM-5 samples with Si/Al = 73 demonstrated that, regardless of the pH of ion exchange, the state of univalent copper occurs when the Cu^+ cation is simultaneously bound to aluminum and silicon cations via oxygen (an absorption band at 2157 cm^{-1} in the spectra taken at room temperature and absorption bands at 2151 and 2177 cm^{-1} at -196°C (Figs. 3a, 3b)). Moreover, Cu^{2+} cations were

Table 4. Binding energies and Cu/Si atomic ratios in CuZSM-5 catalysts (Si/Al = 73) according to XPS data

[Cu], wt %	pH	Cu/Si, atom/atom		E_b ($\text{Cu } 2p_{3/2}$), eV
		calculation	XPS data	
1.26	6	0.008	0.014	933.8
2.19 (fresh)	10	0.030	0.13	935.5
2.64 (fresh)	10	0.016	0.14	935.9
3.53 (after storage)	10	0.022	0.24	935.5

detected in all samples at only -196°C (an absorption band at 2192 cm^{-1}). It is likely that they form CuO clusters. In the samples prepared at pH ~ 10 , Cu^+ cations were additionally detected on the surface of CuO clusters (an absorption band at 2137 cm^{-1}). An absorption band at 2169 cm^{-1} , which was observed at the low temperature in all samples, can be attributed to CO adsorbed on zeolite hydroxyl groups.

Figure 3c demonstrates the spectra of CO adsorbed on the catalyst prepared at pH ~ 10 after storage for 1.5 years. In addition to the absorption bands due to CO adsorbed on Cu^+ cations (2157 and 2177 cm^{-1}), an intense absorption band appeared in the region $2130\text{--}2140\text{ cm}^{-1}$ at room temperature. This band corresponds to CO adsorbed on the surface of a CuO phase.

Moreover, a new intense absorption band at 2149 cm^{-1} , which appeared even at room temperature, was detected. It is believed that this band corresponds to CO adsorbed on copper associates containing Cu^+ and Cu^{2+} (Fig. 3c).

With consideration for published data on the integrated absorption coefficients of CO adsorbed on copper cations [22, 26], we calculated the amounts of copper in different states and their contributions to the total copper content (ΣCu) as determined by chemical analysis. Conclusions that can be drawn from the results presented in Table 5 are given below.

In the catalysts prepared at pH ~ 6 , copper occurs as the following species:

Cu^+ simultaneously bound to Al^{3+} and Si^{4+} via oxygen (2157 cm^{-1});

Cu^{2+} in CuO clusters (2192 cm^{-1}), detected only by CO adsorption at -196°C .

In the catalysts freshly prepared at pH ~ 10 , copper occurs as the following species:

Cu^+ simultaneously bound to Al^{3+} and Si^{4+} via oxygen (2157 cm^{-1});

Cu^{2+} in CuO clusters (2192 cm^{-1}), detected only by CO adsorption at -196°C ;

Cu^+ on the surface of CuO clusters (2137 cm^{-1}).

The storage of the catalyst prepared at pH ~ 10 results in the following:

³ We also thank E.A. Paukshtis for his participation in the discussion of results.

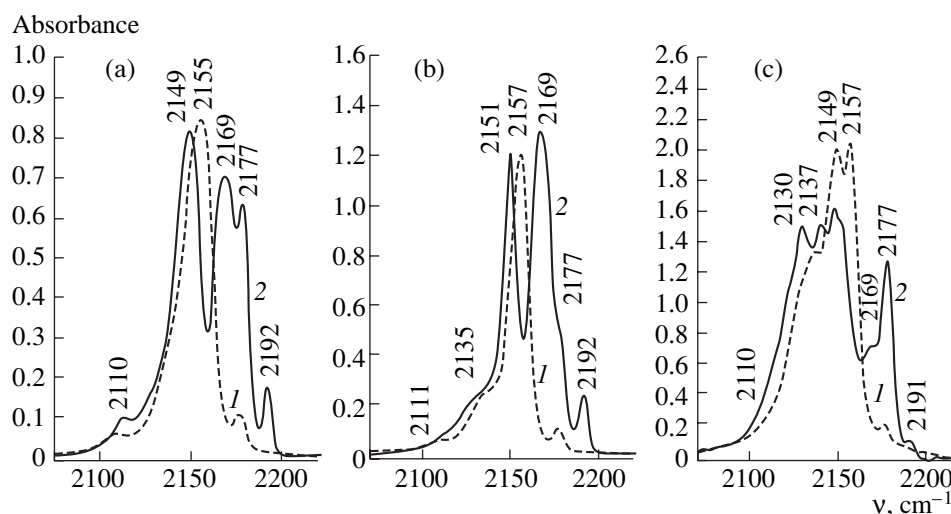


Fig. 3. IR spectra of CO adsorbed on CuZSM-5 (Si/Al = 73) (1) at room temperature and (2) at -196°C : (a) fresh catalyst, $[\text{Cu}] = 1.00\%$, pH ~ 6 ; (b) fresh catalyst, $[\text{Cu}] = 3.53\%$, pH ~ 10 ; and (c) catalyst after aging, $[\text{Cu}] = 3.53\%$, pH ~ 10 .

the amount of Cu^+ decreases (2157 cm^{-1});

the amount of Cu^+ on the surface of CuO clusters increases (2137 cm^{-1});

associates containing Cu^+ and Cu^{2+} appear (2149 cm^{-1});

Cu^{2+} occurs in CuO clusters (2192 cm^{-1}), as detected only by CO adsorption at -196°C .

A comparison between data on the state of copper (these data were obtained by different techniques) and the activity of catalysts (Table 2, Fig. 1) allowed us to conclude that easily reducible copper cations are primarily responsible for the high activity of freshly prepared samples. They manifest themselves as Cu^+ (2157 cm^{-1}) in the IR spectra of adsorbed CO. However, it is impossible to exclude that the detected Cu^+ ions can be formed from isolated Cu^{2+} cations in the

course of the thermal vacuum treatment of catalysts before measuring the IR spectra (heating at 450°C in a vacuum for 4 h) [27]. Note that the amount of Cu^+ cations (2157 cm^{-1}) was approximately the same in samples with close exchange levels prepared at different pH (Table 5). Moreover, an imbalance between the amount of spectroscopically detected copper and the total copper content (ΣCu) may be indicative of the presence of copper oxides (CuO and/or Cu_2O) in all samples. The amount of these oxides increases with increasing ΣCu , as well as on the aging of catalysts.

Similar results were also obtained for catalysts with the ratio Si/Al = 34.

It is likely that the independence of catalyst activity from exchange level at the levels $\geq 100\%$ (Table 2, Fig. 1) can be due to the attainment of a limiting

Table 5. Distribution of copper over various states in bulk CuZSM-5 catalysts (Si/Al = 73) according to IR-spectroscopic data

State of copper	νCO*, cm ⁻¹	1% Cu; pH ~6; fresh		1.5% Cu; pH ~10; fresh		3.5% Cu; pH ~10; fresh		3.5% Cu; pH ~10; after storage for 1.5 years	
		Concentration of Cu species in the sample							
		μmol/g	Cu/ΣCu**	μmol/g	Cu/ΣCu**	μmol/g	Cu/ΣCu**	μmol/g	Cu/ΣCu**
Cu ⁰ (Cu ⁺)	2110	10	0.06	3	0.01	–	–	6	0.01
Cu ⁺ in CuO	2137	–	–	30	0.13	80	0.15	131	0.24
Cu ⁺ –O–Cu ²⁺	2149	–	–	–	–	–	–	99	0.18
Cu ⁺	2157	65	0.41	78	0.33	213	0.41	69	0.13
ΣCu	–	160	1	235	1	520	1	547	1

* CO adsorption at room temperature.

** Relative to the total Cu content of the sample.

amount of copper in an active state. Thereafter, an excess of copper primarily forms an inactive oxide phase. A decrease in the activity of a catalyst with a high copper content, which was prepared at pH ~10, after long-term storage can also be associated with a change in the state of copper (Table 5). Note that data on the properties of zeolite catalysts as functions of storage time are absent from the literature. Only data on the deactivation of metal zeolite catalysts under reaction conditions (segregation of CuO particles in channels) or upon high-temperature treatment (dealumination of the zeolite structure) are known [6, 20].

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