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Catalytic properties and electronic structure of copper ions in Cu-ZSM-5

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Abstract

The effect of ion exchange conditions, such as Si/Al ratio, precursor copper salt, pH and concentration of the solution, on the catalytic activity in SCR of NO by propane and on the electronic state of copper ions in Cu-ZSM-5 has been studied. The NO conversion in NO SCR by C_3H_8 has been found to reach a maximum value at Cu/Al ratio about 0.37–0.4 and remain constant at higher Cu/Al.

ESR and UV–vis DR spectroscopy have been used to elucidate stabilization conditions of copper ions in Cu-ZSM-5 zeolites as isolated Cu^{2+} ions, chain copper oxide structures and square-plain oxide clusters. The ability of copper ions for reduction and reoxidation in the chain structures may be responsible for the catalytic activity of Cu-ZSM-5. These transformations of copper ions are accompanied by the observation of intervalence transitions Cu^{2+}–Cu^{+} and CTLM of the chain structures in the UV–vis spectra.

Keywords: Cu-ZSM-5; Copper-exchanged zeolite; Copper electron state; ESR; UV–vis DRS

1. Introduction

The high catalytic activity of metal-substituted zeolites in selective catalytic reduction (SCR) of NO by hydrocarbons has been established in publications by Iwamoto [1] and Held [2]. Due to significant practical importance, a great number of papers devoted to the study of the unique catalytic properties of metal-substituted zeolites and the nature of their active sites have been published thereafter.

At present, it is well known that among metal-substituted zeolites copper-substituted zeolites (Cu-ZSM-5) are the most effective in SCR of NO by C_2–C_4 hydrocarbons in the presence of excess oxygen. The catalytic activity depends on the reaction temperature [3–5], the hydrocarbon used for reduction [1,3], NO/C_xH_y ratio [4,6], oxygen [4,6–8] or water [3] concentration in the feed, and, especially, on the Cu/Al ratio [1,3,5,9]. Overexchanged Cu-ZSM-5 ($Cu/Al > 0.5$) catalysts exhibit superior catalytic activity and stability both in direct decomposition of NO [1,10] and in selective catalytic reduction of NO by hydrocarbons [1,3–5,11,12]. Based on the literature data, the following conclusion can be made. The catalytic activity of Cu-ZSM-5 in NO SCR by hydrocarbons (propane, in particular) increases with the growth of the Cu exchange level and reaches a maximum at Cu/Al ratio close to ~100% [3,4,11]. Further increase of the Cu/Al ratio up to 450% [3,5] does not affect the NO conversion [3,5,11]. However, the practical use of this conclusion remains unproven because many authors report very different conditions (atomic Si/Al ratio [12], precursor copper salt [11], pH of ion exchange solution [5,12], and temperature [12]) for Cu-ZSM-5 preparation.

Various spectroscopic and physicochemical methods are widely used for elucidation of the nature of copper active states in Cu-ZSM-5 catalysts [5,7,11,13–24]. Copper dimers $[Cu–O–Cu]^{2+}$ [10,13,24–28] or bis-$[Cu–\mu–(O)_2–Cu]^{2+}$ [29–34] have been proposed to be active sites in NO decomposition. There are even more debates on the type of active sites of Cu-ZSM-5 catalysts in NO SCR by hydrocarbons. Isolated Cu^{2+} [11,35–37] and Cu^{+} [1,37,38] ions, oxide CuO- and Cu_2O-like clusters [6,39,40], as well as copper dimer $[Cu–O–Cu]^{2+}$ [22] have been suggested to act as active sites in NO SCR by hydrocarbons.

According to the electron spin resonance (ESR) data, copper cations in Cu-ZSM-5 catalysts calcined in air are believed to be isolated Cu^{2+} ions in two types of distorted octahedral coordination: square pyramidal and square-plane [4,14–19]. Isolated Cu^{2+} ions in square pyramidal coordination pre-

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dominate in Cu-ZSM-5 zeolites with low exchange level [14,18,19], while those in square-plane coordination are dominant in catalysts with high Si/Al ratio and/or high copper content [14,18,19].

The formation of copper dimers with extralattice oxygen (ELO) bridges $[Cu–O–Cu]^{2+}$ located at cation-exchange positions of ZSM-5 framework is most likely for overexchanged zeolites [10,13,20,22–24]. Such copper dimers have been proposed on the basis of mass spectrometric analysis of the amount of oxygen removed during thermal treatment in He [21,41]. The low temperature peaks observed during thermal reduction of Cu-ZSM-5 by H_2 or CO have been also accounted for presence of oxocations [24,41]. In a number of papers the authors using UV–vis diffuse reflectance (UV–vis DR) spectroscopy associate strong absorption bands at 22 700 cm^{-1} [27,37,42] and eventually at 31 200 cm^{-1} [37] with the presence of copper dimers bridged by a single oxygen atom. An ESR signal attributed to $[Cu–O–Cu]^{2+}$ oxocations is observed in Cu–Y [43] and Cu–MOR [14,44], but not in Cu-ZSM-5 [14,17].

The O_2-bridged Cu pairs, $[CuO_2Cu]$, have been originally proposed in a theoretical DFT contribution [45], which showed high stability of such oxocations. The bis-(μ-oxo)dicopper core, $[Cu_2(\mu–O)_2]^{2+}$, is assumed to be characterised by an intense absorption band at 22 700 cm^{-1} and a relatively weaker band at 30 000 cm^{-1} in the UV–vis DR spectra [31–34], while no corresponding ESR signal is detected [31,33].

Recently, we have shown that in addition to isolated Cu^{2+} ions and oxide clusters, calcined Cu-ZSM-5 catalysts contain chain-like $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$ structures located inside the zeolite channels [46–48]. These chains are stabilized by water molecules coordinated in the equatorial (xy) plane around the copper ions (z-axis is along the chains). Due to a strong exchange interaction between Cu^{2+} ions, these chains cannot be observed in the ESR spectra of calcined Cu-ZSM-5 samples. However, they are precursors of chain-like structures observed by ESR [46] and UV–vis DR [47,48] spectroscopy after heat treatment under vacuum at 150–400 °C. The dehydration leads to stabilization of chain-like $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$ structures with coordination number (c.n.) = 2 inside the zeolite channels. The chain-like structure with c.n. = 2 have characteristic charge transfer ligand-to-metal (CTLM) transitions that are red shifted relative to CTLM transitions typical for copper-oxide clusters (18 000–23 000 and 28 000–30 000 cm^{-1}, respectively) [47,48]. Quantum chemical analysis of such chains proves the appearance of CTLM transitions in the low frequency region [47]. Recently, similar linear bi- and polynuclear oxo/hydroxocomplexes have been proposed for stabilization of iron inside the channels of Fe-ZSM-5 on the basis of Mössbauer spectra [49].

The redox properties of Cu-ZSM-5, in particular the capability for reduction of Cu^{2+} to Cu^{+} in the absence of nitrogen oxide, remain an open question. Using ESR, XANES and photoluminescent measurements, it has been shown that paramagnetic Cu^{2+} cations (spin S = 1/2, d^9-ion) are reduced to diamagnetic Cu^{+} cations (S = 0, d^{10}-ion) during heat treatment above 400 °C under vacuum [13,18,20,21,23] or in helium flow [24]. A similar effect is also observed in CO [23] and NO [22] atmosphere at lower temperatures. On the other hand, high stability of isolated Cu^{2+} ions in Cu-ZSM-5 zeolites to reduction during vacuum heat treatment has been noticed in a number of papers [11,14,36,50]. Although both types of copper cations (Cu^{2+} and Cu^{+}) are present in active catalysts, the literature lacks direct evidence for participation of these sites either in NO decomposition or NO SCR by hydrocarbons.

Summarizing a number of experimental studies, the presence of isolated Cu^{2+} ions stabilized by oxide ligands in cation-exchanged sites of the zeolite matrix has been definitely proven. These Cu^{2+} ions are not reduced under mild conditions (especially at low temperatures) due to the ionic nature of the Cu–O bond typical for these species. Although the structure of copper oxocations with extralattice oxygen is not clear, they possess redox properties and account for the catalytic activity of Cu-ZSM-5 catalysts. Probably, these structures have a high covalence of the bond between Cu^{2+} ions and ELO and a low distance between two Cu^{2+} ions facilitating the electron transfer during reduction.

The Cu-ZSM-5 activity depends on the microstructure and the copper content, which are determined by ion exchange conditions. The literature data show essential differences between the main states of copper ions and their ratio even at similar ion exchange levels because different methods are used for copper incorporation into the zeolites. There has been no systematic study of the effects of preparation and thermal treatment conditions on the peculiarities of copper stabilization in Cu-ZSM-5, which are important for understanding the nature of the active sites and optimization of the catalyst composition.

The present work summarizes the results of the investigation of the Cu-ZSM-5 catalytic activity in SCR NO by propane depending on the ion exchange conditions (pH of copper solution, copper precursor, Si/Al ratio, temperature etc.) and copper loading (0.3–2.7 wt.%). ESR and UV–vis DR spectroscopy have been used to elucidate the stabilization conditions of copper ions in Cu-ZSM-5 zeolites as isolated Cu^{2+} ions, chain-like copper oxide structures and square-plain oxide clusters. Most interesting among the above states of copper ions are the chain structures $Cu^{2+}–O^{2-}–Cu^{2+}–O^{2-}$ due to the easiness of copper reduction and reoxidation and their ability to stabilize bonded states of copper ions with mixed valence $Cu^{2+}\cdots Cu^{+}$.

2. Experimental

2.1. Parent zeolite

Three types of H-ZSM-5 zeolites with Si/Al atomic ratio 17, 30 and 45 were used. The physicochemical properties of these parent samples had been studied earlier [5] and are presented in Table 1. The chemical composition of the parents was determined by X-ray fluorescence spectroscopy using a VRA-20R analyzer. The good crystallinity and purity of the parent samples was confirmed by collecting X-ray diffraction (XRD) patterns using an HZG-4C diffractometer with Cu Kα

Table 1
Physicochemical properties of parent zeolites

No.	Parent	Chemical composition (wt.%)							Si/Al	S_{BET} (m^2/g)	S_{extern} (m^2/g)	V_Σ (cm^3/g)	V_{micro} (cm^3/g)
		Al	Si	K	Na	Mg	Ca	Fe					
1	H-ZSM-5-17	2.16	39.60	0.02	0.05	0.02	0.04	0.09	17	385	104	0.200	0.122
2	H-ZSM-5-30	1.43	42.89	0.01	0.06	0.03	0.04	0.65	30	450	166	0.255	0.125
3	H-ZSM-5-45	0.97	43.35	0.01	0.00	0.03	0.06	0.60	45	346	127	0.239	0.095

radiation. The morphology of the parent samples was characterized using scanning electron microscopy with an REM-100U electron microscope. According to the scanning electron microscopy data, the zeolite samples consist of regular coffin-shaped crystals without amorphous phase. The presence of extralattice Al^{3+} ions was confirmed by ^{27}Al NMR using a Bruker MSL-400 spectrometer with a magnetic field strength of 9.4 T. The extralattice Al^{3+} content was about 10% of the total aluminum content for the sample with Si/Al = 17, and no extralattice Al^{3+} was detected in the other samples. N_2 adsorption–desorption isotherms were measured at 77 K using an ASAP-2400 analyzer. The specific surface areas (S_{BET}) of the zeolite samples were determined from the linear part of BET plot, while the micropore volume (V_{micro}) and the external crystallite surface area were determined by *t*-method from desorption isotherms. The pore structure parameters are typical for H-ZSM-5 structure.

2.2. Preparation of Cu-ZSM-5 samples

The first series of catalysts were prepared by ion exchange of the H-ZSM-5 samples with aqueous (pH ~6) and ammonia (pH ~10) solutions of copper acetate at room temperature according to [5]. The copper salt concentration in the ion-exchange solution was varied from 0.4 to 8 mg Cu/ml. The slurry concentration (the ratio of solution volume to zeolite mass, *S*/*Z*) was 10, 30 and 50. After 48 h of ion exchange the zeolite samples were filtered and washed with distilled water. All the samples were dried at 110 °C and calcined in air at 500 °C. Such samples will be hereafter denoted as ‘‘calcined samples’’.

The second series of catalysts were prepared by ion exchange of the H-ZSM-5 samples with aqueous solutions of copper nitrate (pH ~4), copper sulphate (pH ~4) and copper chloride (pH ~4) at room temperature. The copper salt concentration in the ion-exchange solution was 8 mg Cu/ml, the slurry concentration was 10. Other preparation conditions were identical to those described above.

The third series of catalyst were prepared by ion-exchange of the H-ZSM-5-30 samples with aqueous copper acetate solutions acidified by acetic anhydride, nitric, sulphuric or hydrochloric acid up to pH 4.6. The concentration of copper acetate in the ion-exchange solution was 4 mg Cu/ml, the slurry concentration was 10. Other preparation conditions were identical to those described above.

Alternatively, Cu-ZSM-5 samples were prepared by ion exchange of the H-ZSM-5 samples with an aqueous solution of copper nitrate (pH ~4, 8 mg Cu/ml) at 80 °C according to [12]. The samples were washed after the ion exchange and were subjected to thermal treatment at similar conditions.

The copper contents of Cu-ZSM-5 samples were determined by inductively coupled plasma (ICP) method. The copper content in the samples was varied from 0.3 to 2.7 wt.%. The zeolite exchange level (Cu/Al, in %) was calculated as 2 × 100% × Cu/Al_{at} from the chemical analysis data [13]. This formula is based on assumption that stoichiometric ion-exchange is reached when one Cu^{2+} ion compensates the exchange of two framework aluminum atoms. In this case, the maximum value of the exchange level is 100% (or $Cu/Al_{at} = 0.5$). The samples are denoted as *n*% Cu-ZSM-5-*X*–*Y* where *n*% is copper content (%), *X* is the atomic Si/Al ratio, and *Y* is the exchange level (%).

For heat treatment under vacuum, a Cu-ZSM-5 sample was placed into a quartz glass cell (~0.5 g) or quartz glass ampoule (~30–35 mg), heated at 500 °C in air, cooled to room temperature and evacuated at 25, 150, 300 and 400 °C for 1 or 4 h. In selected experiments the samples were evacuated for longer periods of time up to 20 h. These samples will be denoted as ‘‘evacuated samples’’.

2.3. ESR and UV–vis DR measurements

The ‘‘calcined’’ and ‘‘evacuated’’ samples were studied by ESR and UV–vis DR spectroscopy.

The ESR spectra were recoded using a Bruker spectrometer ($\lambda = 3$ cm) at 77 and 300 K in quartz glass ampoules with an internal diameter of 3 mm. The parameters of the ESR spectra were determined by comparison with the spectrum of a DPPH standard ($g = 2.0037 \pm 0.0002$).

The UV–vis DR spectra were obtained at room temperature using a ‘‘Shimadzu’’ UV-2501 PC spectrophotometer equipped with a diffuse reflectance accessory (ISR-240 A). The spectra were recorded against a $BaSO_4$ reflectance standard in the range of 900–190 nm. The UV–vis DR spectra are shown as the Kubelka–Munk representation, *F*(*R*).

2.4. Catalytic experiments

The activity of the Cu-ZSM-5 catalysts was tested in NO reduction with propane. The space velocity of gas flow was 42 000 h^{-1}, the temperature range was 200–500 °C, the gas mixture had the following composition: NO 300 ppm, C_3H_8 0.15 vol.%, O_2 3.5 vol.%, N_2 balance. The activity of the catalysts was characterized by the NO conversion (X_0, %) at a preset temperature. The catalytic activities normalized per 1 g Cu (W, mol/g_{Cu} min) at 350 °C were estimated for comparison of the catalysts.

To understand the iron influence on the catalytic properties of Cu-ZSM-5 catalysts, the parent zeolite samples containing iron as an impurity were studied in NO SCR by propane. NO conversion on the parent zeolites with Si/Al ratios equal to 17, 30 and 45 was found to be 5–7% at 300–500 °C [5].

3. Results and discussion

3.1. Influence of ion-exchange conditions on copper content and Cu/Al ratio in Cu-ZSM-5

According to the literature data, the parameter determining the catalytic activity of Cu-ZSM-5 catalysts and their stability to deactivation by oxygen, water vapour and sulphur compounds is the Cu/Al ratio. It can be varied in a wide range (up to 450%) depending on the preparation conditions. The effects of ion exchange conditions: zeolite Si/Al ratio, copper salt precursor, concentration and pH of copper acetate solution, *S*/*Z* ratio, and ion exchange temperature on the Cu/Al ratio in Cu-ZSM-5 and their catalytic activity in SCR of NO by propane have been studied.

At selected ion exchange conditions, an increase of the *S*/*Z* ratio from 10 to 50 had been earlier found to have a negligible effect on the Cu/Al ratio in Cu-ZSM-5 [5]. When the aqueous copper acetate solutions with concentration in the range of 0.4–8 mgCu/ml and pH ∼6 were used for Cu-ZSM-5 preparation, the maximum achievable level of Cu exchange with H-ZSM-5 was 75–100%. In this case, the exchange level is determined mainly by the copper concentration in the solution and by the zeolite Si/Al ratio (Fig. 1A). At identical Si/Al ratios, the copper content in Cu-ZSM-5 samples and, hence, the Cu/Al ratio decreased with dilution of the copper acetate solutions (from 8 to 0.4 mgCu/ml). At identical solution concentration, a trend for an increase of the Cu/Al ratio with the Si/Al ratio increase has been observed.

At the same copper salt concentration range in the ion-exchange solution (0.4–8 mgCu/ml), the use of ammonia copper acetate solution (pH ∼10) allowed for broader variation of the Cu/Al ratio and a higher achievable level of Cu exchange with H-ZSM-5 (up to 300%). The exchange level increased with the copper concentration in solution and the zeolite Si/Al ratio (Fig. 1B). This increase was more pronounced compared to the aqueous solution. The achievable level of Cu exchange with H-ZSM-5 was 90–108, 64–135 and 114–309%, for the samples with Si/Al = 17, 30 and 45, respectively.

The copper content and Cu/Al ratio for the second series of Cu-ZSM-5 samples prepared by the ion-exchange of H-ZSM-5 with aqueous solutions of different copper precursors are summarized in Table 2. The copper salt precursor has been shown to affect the copper content in Cu-ZSM-5 samples. At the same concentration of the aqueous copper salt solution, the copper content and, consequently, the Cu/Al ratio in Cu-ZSM-5 samples prepared from copper acetate was noticeably higher (∼2–3 times) than in the samples prepared from copper nitrate, sulphate, or chloride (N1 and 3–5; N7 and 9–11, Table 2). Similar to the samples prepared using copper acetate, the Cu/Al ratio in the Cu-ZSM-5-30 samples had been earlier shown to increase with the copper nitrate concentration in the solution [51]. However, when aqueous copper acetate solution was used for ion-exchange with H-ZSM-5-30, the Cu/Al ratio close to the one theoretically possible for ionic exchange (Cu/Al = 75–100%) was achieved at solution concentration in the range of 4–8 mg Cu/ml. When aqueous copper nitrate solutions were used, the Cu/Al value in Cu-ZSM-5-30 samples did not exceed 50% even for more concentrated solutions (16–24 mg Cu/ml) [51]. To achieve a higher Cu/Al ratio in the samples prepared from copper nitrate it was necessary to repeat the ion-exchange procedure 2 or 3 times. Certain increase of the copper content (from 0.36 to 0.54 wt.%, N9 and N13, Table 2) in Cu-ZSM-5 samples was observed when elevated temperature (80 °C) were used the ion-exchange.

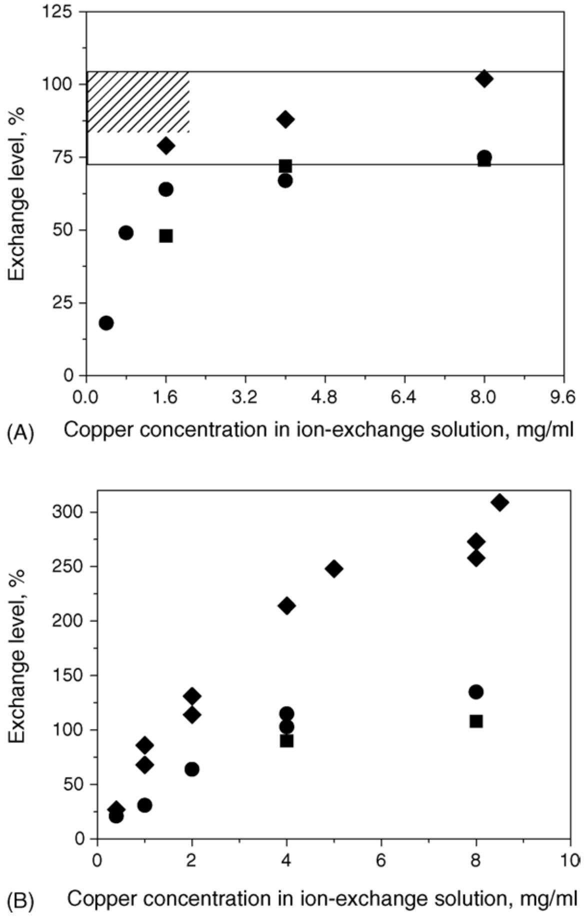

Fig. 1. Exchange level in Cu-ZSM-5 vs. copper concentration in ion-exchange solution depending on precursor copper salt (A, copper acetate, pH ∼6; B, ammonia copper acetate, pH ∼10) and Si/Al ratio (■, 17; ●, 30; ◆, 45).

The aqueous solutions of copper nitrate, sulphate, and chloride have low pH (∼4). This can be the cause of the low copper content in the samples prepared using these solutions. To check the effect of the solution pH, the third series of catalyst was prepared by ion-exchange of H-ZSM-5-30 with aqueous copper acetate solution acidified by acetic anhydride, nitric, sulphuric or hydrochloric acid to pH 4.6. One can see (Table 2) that, regardless of the acidic anion, these samples (N15–18) are characterised by the Cu/Al ratio 61–66%,which is

Table 2
The ion-exchange conditions and data of elemental analysis and catalytic activity of Cu-ZSM-5 samples

No.	Parent of H-ZSM-5	Properties of ion-exchange solution			Properties of Cu-ZSM-5 samples		Catalytic activity in DeNO*x*-C_3H_8		
		Copper precursor	Concentration (mg Cu/ml)	pH	Copper content (wt.%)	Exchange level (%)	NO conversion (%) at		*W* (10^{-4} mol NO/g_{Cu} min, at 350 °C)
							350 °C	400 °C	
1	H-ZSM-5-17	$Cu(CH_3COO)_2$	8	5.7	1.88	74	69	78	3.9
2	H-ZSM-5-17	$Ac(NH_4OH)$	8	10.4	2.75	108	58	85	2.0
3	H-ZSM-5-17	$Cu(NO_3)_2$	8	4.1	0.99	38	47	55	4.0
4	H-ZSM-5-17	$CuSO_4$	8	4.0	1.24	48	34	39	2.2
5	H-ZSM-5-17	$CuCl_2$	8	4.1	1.03	40	53	66	4.1
6	H-ZSM-5-17	$Cu(CH_3COO)_2$	2	5.8	1.24	48	60	75	4.8
7	H-ZSM-5-30	$Cu(CH_3COO)_2$	8	5.7	1.26	75	70	85	5.9
8	H-ZSM-5-30	$Ac(NH_4OH)$	8	10.4	2.27	135	65	90	2.9
9	H-ZSM-5-30	$Cu(NO_3)_2$	8	4.3	0.36	21	24	47	5.8
10	H-ZSM-5-30	$CuSO_4$	8	4.0	0.45	26	24	30	3.4
11	H-ZSM-5-30	$CuCl_2$	8	4.1	0.57	34	33	40	4.3
12	H-ZSM-5-30	$Cu(CH_3COO)_2$	1	5.9	0.33	20	34	49	6.8
13[a]	H-ZSM-5-30	$Cu(NO_3)_2$	8	4.3	0.54	32	48	60	3.8
14	H-ZSM-5-30	$Cu(CH_3COO)_2$	4	5.8	1.10	65	71	87	6.3
15	H-ZSM-5-30	$Ac(CH_3COOH)$	4	4.6	1.12	66	70	85	6.6
16	H-ZSM-5-30	$Ac(HNO_3)$	4	4.6	1.03	61	53	66	4.3
17	H-ZSM-5-30	$Ac(H_2SO_4)$	4	4.5	1.00	59	37	49	2.8
18	H-ZSM-5-30	Ac(HCl)	4	4.6	1.04	61	40	49	3.0
19	H-ZSM-5-45	$Cu(CH_3COO)_2$	8	5.7	1.16	102	70	90	7.9
20	H-ZSM-5-45	$Ac(NH_4OH)$	8	10.4	2.94	258	71	89	3.2

$Ac(NH_4OH)$, ammonia copper acetate solution; $Ac(CH_3COOH)$, copper acetate solution acidified by acetic anhydride; $Ac(HNO_3)$, copper acetate solution acidified by nitric acid; $Ac(H_2SO_4)$, copper acetate solution acidified by sulfuric acid; Ac(HCl), copper acetate solution acidified by hydrochloric acid.

[a] Samples prepared by ion-exchange at 80 °C.

close to the ones obtained for samples prepared from copper acetate solution with pH ~5.8 (N14).

The lower exchange level obtained after the ion-exchange of H-ZSM-5 with the copper nitrate, sulphate or chloride solutions compared to the copper acetate solution demonstrates that the precursor copper salt predetermines the state of copper ions in the solution and affects the ion-exchange process. The ratio of hydrated Cu^{2+} cations to partially hydrolyzed copper complexes is known to be changed with the hydrolysis degree depending on temperature, pH and concentration of the solution [52,53]. The composition of the formed copper hydroxocomplexes is also determined by the concentration and pH of the copper salt solution [52,53]. The formation of binuclear hydrolysis products $[Cu_2(OH)_2{}^{2+}]_{aq}$ in solutions with concentration of 10^{-3}–0.1 M was observed to start at pH ~5 [52], their concentration reaching 10–40% [52]. Meanwhile, in low-concentrated solutions (10^{-4} to 10^{-5} M) at pH ~8, hydrolysis yields $[Cu(OH)]^{+}{}_{aq}$ [52]. Copper acetate solutions in the chosen concentration range (0.025–0.125 M) are characterized by pH ~5.75–6.2, slightly decreasing (to 5.0–5.15) after the ion exchange. The comparison of the experimentally observed pH values of the initial copper acetate solution and the mother liquor solution with the published data [52] shows that the participation of binuclear hydroxocomplexes $[Cu_2(OH)_2{}^{2+}]_{aq}$ in the ion exchange is possible. Copper nitrate, sulphate and chloride solutions in the same range of concentration have pH ~4–4.3. So, copper ions take part in the ion-exchange as hydrated mononuclear ions $[Cu(H_2O)_6]^{2+}$ and $[Cu(OH)(H_2O)_5]^{+}$.

Ion exchange values exceeding the theoretically possible one (samples N2, 8, 20, Table 2) are clearly observed when Cu-ZSM-5 samples are prepared from ammonia copper acetate solutions (pH ~10). This tendency is noted to grow when both the Si/Al ratio and the copper acetate concentration in solution increase. Mono-, and bi-nuclear copper cations of various compositions (for example, $[Cu_2(OH)_2{}^{+}]_{aq}$), as well as $[Cu_3(OH)_4]^{2+}$ cations produced in low-concentrated solutions ($<10^{-3}$ M, [53]), can participate in the ion exchange in this case. Furthermore, the ion exchange between H-ZSM-5 and ammonia copper solution can be hindered by sedimentation of amorphous copper hydroxide after the pH decrease to ~8–9 [54] during the ion exchange and washing.

These reasons can increase the calculated ion exchange level and lead to stabilization of some copper ions in positions different from the zeolite cation-exchange sites.

3.2. Effect of ion-exchange conditions on the catalytic activity of Cu-ZSM-5

The catalytic activities of Cu-ZSM-5 samples of three series with Si/Al = 17, 30 and 45 have been studied. The NO conversion in NO SCR by C_3H_8 was found to reach a maximum value at the exchange level of about 75–100% (Fig. 2) independent of the way this exchange level was reached: either by varying the copper content (Fig. 2A and B) or the Si/Al ratio (Fig. 2B). Besides, for catalysts characterised by identical Si/Al ratios and copper contents, the NO conversion was independent

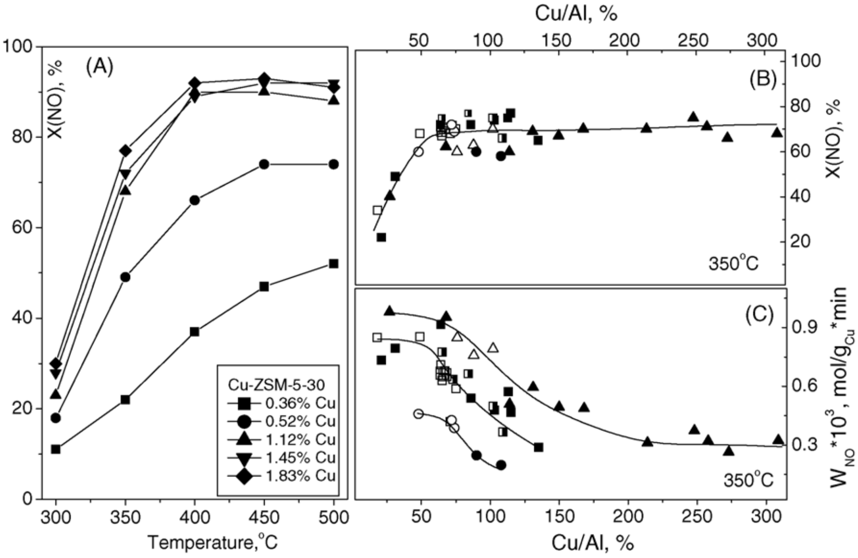

Fig. 2. NO conversion (A, B) and catalytic activity (C) of Cu-ZSM-5 with different copper contents versus temperature (A) and Cu/Al ratio (B, C). The samples were prepared by ion exchange of copper acetate solution with pH ∼4.6 (⊞), ∼6 (○, □, △), ∼10 (●, ■, ▲) with H-ZSM-5 zeolites characterized by Si/Al ratio equal to 17 (○, ●), 30 (⊞, □, ◨, ■) and 45 (△, ▲). The samples (◨) were prepared by ion exchange procedure at pH ∼6 repeated thrice.

of the copper acetate solution pH (Fig. 2B) used for the ion-exchange. For example, the 1.1%Cu-ZSM-5-30-75 samples prepared from copper acetate solution with pH 4.2–4.6, 5.75 and 10.4 (adjusted by acetic anhydride or using aqueous and ammonia solutions, respectively) showed 70% of NO conversion at 350 °C and 85% of NO conversion at 400 °C. The NO conversion remained constant at higher Cu/Al (up to 309%). The absolute values of the maximum NO conversion were found to depend on the reaction temperature, reaching 22–30 at 300 °C, 65–77% at 350 °C, and 85–97% at 400–500 °C (Fig. 2A).

The catalytic activity of Cu-ZSM-5 samples in NO SCR by C_3H_8 has been shown to depend on the precursor copper salt used for the preparation. At the same Cu/Al ratio in Cu-ZSM-5 samples, the activity of the samples prepared from copper acetate was higher than for the samples prepared from copper nitrate, sulphate, and chloride (N6 and 3–5; N12 and 9–11, Table 2). For example, the NO conversion at 350 °C on 1.24%Cu-ZSM-5-17-48 samples prepared using copper acetate (N6, Table 2) and copper sulphate (N4, Table 2) was 60 and 34%, respectively. Similar results were also observed for samples with Si/Al = 30. 0.33%Cu-ZSM-5-30-20 sample prepared from copper acetate solution was more active (X_{NO} = 34% at 350 °C) than 0.45%Cu-ZSM-5-30-26 sample prepared from copper sulphate solution (X_{NO} = 24% at 350 °C).

The influence of the precursor copper salt on the catalytic activity in NO SCR by C_3H_8 is also confirmed by the experimental data for samples prepared from copper acetate solution acidified by various additives to pH ∼4.6. When acetic anhydride was used for lowering pH of the copper acetate solution (N15, Table 2), the activity did not change compared to Cu-ZSM-5 sample prepared at pH ∼5.8 (N14, Table 2). The lowering of the copper acetate solution pH (N14, Table 2) by adding nitric, sulphuric or hydrochloric acids (N16–18, Table 2) led to a decrease of the Cu-ZSM-5 activity, whereas the copper content and Cu/Al ratio in Cu-ZSM-5 samples were not changed.

The dependence of the NO conversion on the Cu-exchange level presented in Fig. 2B agrees with the experimental data reported in numerous papers [3,4,8,11,55,56]. Thus, the catalytic activity of Cu-ZSM-5 in NO SCR by C_3H_8 was shown to increase with the growth of the exchange level from 50 to 100% and remain unchanged with the further growth (up to 450%) [3]. The NO SCR by C_3H_8 and NO SCR by C_3H_6 activities of Cu-ZSM-5 catalysts with the exchange level in the range of 90–150% were nearly the same [4].

The use of aqueous copper acetate solution with pH ∼6 has been found to be preferable because it allows for preparation of Cu-ZSM-5 with Cu/Al ∼100% at lower concentration (4–8 mg/ml) than aqueous solutions of other copper salts (nitrate, sulphate or chloride). In this case, the higher maximum values of the catalytic activity in NO SCR by C_3H_8 are obtained irrespective of the Si/Al ratio. Moreover, the use of an aqueous copper acetate solution is preferred from the practical viewpoints because this solution is not toxic and has nearly neutral pH ∼6 in a wide concentration range.

3.3. ESR and UV–vis DR spectra of Cu-ZSM-5 catalysts calcined at 500 °C

ESR and UV–vis DR spectroscopy have been used to establish the basic conditions for stabilization of the three states of copper in Cu-ZSM-5 samples: isolated Cu^{2+} ions, O-bridged copper pairs and square-plain oxide clusters.

We have previously shown for a series of Cu-ZSM-5 samples with Si/Al = 30 that these samples calcined in air at 500 °C contain isolated Cu^{2+} ions, irrespective of the preparation method [48] and copper concentration [46]. All Cu-ZSM-5 samples exhibit an axial ESR spectrum of Cu^{2+} ions at 77 K with resolved hyperfine structure (HFS) with $g_{\parallel}$ = 2.39,

$g_\perp = 2.08$, and $A_\parallel = 130$ G (Fig. 3A, curve 2). The UV–vis DR spectra of these catalysts are characterized by an absorption band (a.b.) at 12 500 cm^{-1} (Fig. 3B, curve 2). The analysis of the parameters of ESR and UV–vis DR spectra indicates that these spectra are typical for isolated Cu^{2+} ions with $d_{x^2-y^2}$-ground state stabilized in octahedral crystal fields with small tetragonal distortion, which are created by oxide ligands. In this case, the band at 12 500 cm^{-1} is close by energy to d–d transitions between T_{2g} and E_g terms in $[Cu(H_2O)_6]^{2+}$ hexaaquacomplexes [57]. These results are in a good agreement with the abundant literature data on the ESR and UV–vis DR spectra of Cu^{2+} ions in various hydrated zeolites [14,44,58], including ZSM-5 zeolites [11,14,16,18,24].

The copper content in Cu-ZSM-5 samples found by the chemical analyses was 0.3–1.5 wt.%. Meanwhile, the copper concentrations derived from the ESR data did not exceed 50–60% of the actual concentration. The fraction of ESR-detectable copper decreased with increasing copper loading and it did not exceed 10–30% at higher loadings. At the same time, the intensity of a.b. at 12 500 cm^{-1} slightly grew with an increase of the copper content from 0.3 to 2.5 wt.% (exchange levels 18 and 147%, respectively) [47].

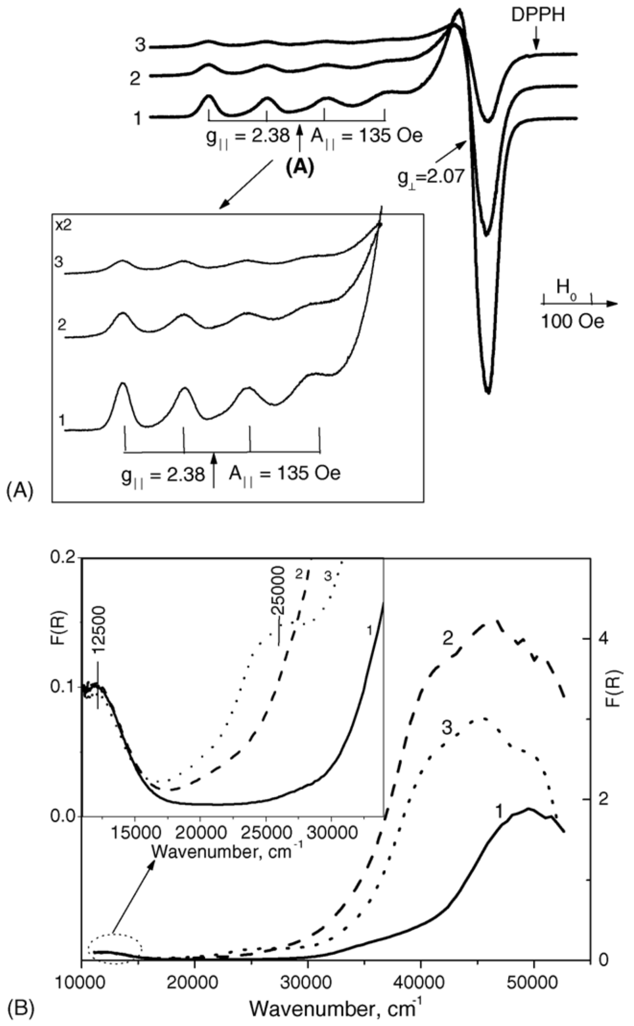

Fig. 3. ESR spectra (77 K, A) and UV–vis DR spectra (B) of calcined Cu-ZSM-5 catalysts 1.1%Cu-ZSM-5-17–45 (curve 1), 1.2%Cu-ZSM-5-30-71 (curve 2) and 1%Cu-ZSM-5-45-88 (curve 3) prepared by ion exchange with aqueous copper acetate solution (pH ∼6).

The ESR and UV–vis DR spectra of three calcined Cu-SZM-5 samples characterized by similar copper contents (1–1.2 wt.%) and different Si/Al ratios are presented in Fig. 3. One can be see that their ESR parameters and absorption bands in the visible region (12 500 cm^{-1}) are nearly identical. Besides, calcined Cu-ZSM-5 samples exhibit the zeolite matrix fundamental absorption edge around 35 000–37 500 cm^{-1} in the UV–vis DR spectra (Fig. 3B). It is attributed to the gap typical for dielectric metal-oxide structures. An absorption band at 25 000 cm^{-1} (Fig. 3B, curve 3) in the UV–vis spectra of 1%Cu-ZSM-5-45–88 is attributed to CTLM of iron oxide clusters in H-ZSM-5-45. CTLM bands of copper oxide clusters (axial or square-plane dimer) can be observed in the same region (around 27 000–30 000 cm^{-1} [57]). This CTLM band can hardly be seen in the UV–vis DR spectra of calcined Cu-ZSM-5 samples, although its appearance as a shoulder on the fundamental absorption edge can result in an apparent low-frequency shift of the latter (Fig. 3B, curve 2 and 3). This shift is more pronounced for Cu-ZSM-5 samples prepared from ammonia copper acetate with a high copper content (>2 wt.%) and a high Si/Al ratio.

The correlation between the ESR and UV–vis data for these samples has shown that the higher is the Si/Al ratio, the lower is the content of isolated Cu^{2+} ions ($g_\parallel = 2.39$, $g_\perp = 2.08$, $A_\parallel = 135$ Oe) and the higher is the content of copper ions stabilized in square-plain oxide clusters (CTLM band at 30 000–32 000 cm^{-1}). This is an expected result because an increase of the zeolite Si/Al ratio leads to a decrease of the number of ion exchange sites, and, consequently, the concentration of isolated Cu^{2+} ions. The same dependencies were also observed for the samples with a high copper content (2.4–2.7 wt.% Cu) prepared from ammonia copper acetate solutions. However, in this case the fraction of ESR-detectable copper was lower than the one for samples prepared from aqueous copper acetate solutions and containing 1–1.2 wt.% Cu. This conclusion agrees well with the data obtained by chemical analysis, indicating that the higher is the Si/Al ratio, the less Cu^{2+} ions are washed out by re-exchange of Cu-ZSM-5 samples with ammonia chloride solution (Table 3). Isolated Cu^{2+} ions are known to be washed out from calcined samples under re-exchange conditions.

As we discussed earlier [5], the presence of copper oxide clusters in Cu-ZSM-5 was confirmed by FTIR of adsorbed CO and XPS. The absorption band observed in the FTIR spectra of Cu-ZSM-5 at 2192 cm^{-1} can be attributed to complexes of CO with isolated or weakly associated Cu^{2+} ions in CuO clusters [5]. An additional adsorption band at 2137 cm^{-1} was observed in the samples prepared from ammonia copper acetate solution (at pH ∼10) and attributed to CO adsorbed on Cu^{2+} cations located on the surface of copper oxide clusters. The concentration of these copper states grows with the increase of the copper content in the samples. Besides, the copper content observed by FTIR and its total content do not match. This is an evidence of the presence of copper oxide clusters in all the samples. A comparison of bulk and surface Cu/Si ratios

Table 3
Copper content in Cu-ZSM-5 before and after re-exchange with ammonia chloride solution (1 M solution, 25 °C, 2 h)

No.	Samples	pH	Copper content (wt.%) and Cu/Al				$(Cu_0–Cu_1)/Cu_0$ (%)	Catalytic activity in DeNOx-C_3H_8 at 350 °C			
			Initial		Re-exchanged			Initial		Re-exchanged	
			Cu_0 (wt.%)	Cu/Al (%)	Cu_1 (wt.%)	Cu/Al (%)		X(NO) (%)	W (10^{-4} mol NO/g_{Cu} min)	X(NO) (%)	W (10^{-4} mol NO/g_{Cu} min)
1	1.88%Cu-ZSM-5-17-80	6	1.88	80	0.14	6	92.5	69	3.9	7	–
2	1.24%Cu-ZSM-5-30-74	6	1.24	74	0.08	4	93.5	71	6.1	12	–
3	0.93%Cu-ZSM-5-45-82	6	0.93	82	0.07	6	92.5	65	7.3	17	–
4	2.74%Cu-ZSM-5-17-106	10	2.74	106	0.52	20	80	58	2.0	15	1.9
5	2.27%Cu-ZSM-5-30-135	10	2.27	135	0.99	58	56	65	2.9	20	2.4
6	3.12%Cu-ZSM-5-45-274	10	3.12	274	1.93	170	38	70	3.1	30	3.4

calculated according to the chemical analysis and XPS for Cu-ZSM-5-45 series [5] led us to a conclusion that the states of copper in the samples prepared from aqueous copper acetate solution at pH ~6 (Cu/Si is equal to 0.013 and 0.014, correspondingly, for 1.26%Cu-ZSM-5-45-110) are relatively uniform. Bulk and surface Cu/Si ratios differ significantly when solutions with pH ~10 are used (0.022 and 0.13, correspondingly, for 2.19%Cu-ZSM-5-45-192). This fact evidences that copper concentrates on the catalyst surface, probably, due to the formation of copper oxide clusters.

The study of Cu-ZSM-5 samples over a wide range of Cu/Al ratios varied by ion-exchange conditions has shown that two copper states, isolated Cu^{2+} ions ($g_{\|} = 2.38$, $A_{\|} = 135$ Oe and $g_{\perp} = 2.07$, a.b. 12 500 cm^{-1}) and copper oxide clusters (CTLM 30 000–32 000 cm^{-1}) – are observed by the ESR and UV–vis spectroscopy. Part of copper ions are undetectable by ESR and not washed out from Cu-ZSM-5 by re-exchange with ammonia chloride. So far, their structure was not clear. The influence of the vacuum heat pretreatment of Cu-ZSM-5 on the copper states has been studied to give a clear picture.

3.4. ESR and UV–vis DR spectra of Cu-ZSM-5 catalysts evacuated at 25–400 °C

Heat treatment of calcined Cu-ZSM-5 samples under vacuum is well known to result in a significant decrease in the intensity of its ESR spectrum [11,14,16,19,21,46]. The spectra observed at 77 K after such treatment (Fig. 4) are due to a superposition of two anisotropic spectra of Cu^{2+} ions with different parameters (type B: $g_{\|} = 2.33$, $g_{\perp} = 2.07$, $A_{\|} = 145$ G; type C: $g_{\|} = 2.27$–2.28, $g_{\perp} = 2.06$, $A_{\|} = 165$ G) and an ESR spectrum with $g_{\|} = 2.02$ and $g_{\perp} = 2.05$ [46].

Significant changes were observed after the vacuum heat treatment in the UV–vis DR spectra of Cu-ZSM-5 as well [47]. First, the shift of the absorption band corresponding to d–d transitions of isolated Cu^{2+} ions from 12 500 to 13 400 cm^{-1} (type B) or 14 500 (type C) cm^{-1} was shown for all Cu-ZSM-5 samples independent of the ion-exchange conditions. Second, the appearance of intense absorption at 15 000–17 000 and 30 000–32 000 cm^{-1} (Fig. 5, [47]) and several distinct bands in the region of 18 000–23 000 cm^{-1} (Fig. 6, [47,48]) was observed. Their appearance depended on the ion-exchange conditions used for Cu-ZSM-5 preparation and heat vacuum treatment.

The shift of the absorption band in the d–d transition region from 12 500 to 13 400 cm^{-1} was earlier reported for evacuated Cu-ZSM-5 zeolites as a result of dehydration at 100 °C [21]. However, in contrast to our data, in that paper the disappearance of the d–d transition band was observed after evacuation at 400 °C. The disappearance of the band assigned to d–d transitions in isolated Cu^{2+} ions was explained by their reduction to Cu^{+} [21]. Note that, most likely, isolated Cu^{2+} ions are reduced only under severe conditions, for example, in the hydrogen [23] or ammonia atmosphere [59]. The ESR (Fig. 4) and UV–vis spectra (Fig. 5) of Cu^{2+} ions remaining after the vacuum heat treatment correspond to the octahedral coordination of copper with strong tetragonal distortion. The level of the tetragonal distortion is very high for some ions (C: $g_{\|} = 2.27$–2.28, $A_{\|} = 165$ G, $\Delta(T_{2g} - E_g) = 14\,500$ cm^{-1}). That is why it should be described by other methods.

The stabilization of some copper ions as square-plane copper-oxide clusters was also observed after heat vacuum treatment of Cu-ZSM-5 at 400 °C. This complex is characterized by a CTLM band around 30 000–32 000 cm^{-1} in the UV–vis spectra (Fig. 5, curve 5). Their formation is promoted by the use of ammonia copper acetate solutions (pH ~10) and high Si/Al ratio (Si/Al $\geq$ 30). However, it is observed even for samples with Cu/Al close to the one theoretically possible for ion-exchange (~100%). For example, 1.88%Cu-ZSM-5-17-74 samples evacuated at 400 °C for 4 and 16 h exhibit the CTLM band at 30 000 and 32 000 cm^{-1} in UV–vis spectra, respectively (Fig. 7, curves 1 and 2). The shift of the CTLM band of square-plane copper-oxide clusters suggests that its position in the UV–vis spectra depends on the cluster size. The larger is the cluster (up to the formation of a fine CuO crystallite), the more shifted is this CTLM band (Fig. 7, curves 2 and 3). The CTLM band of square-plane clusters can hardly be seen in the UV–vis spectra of evacuated samples with high Cu/Al due to its superposition with the fundamental absorption edge of the zeolite matrix (35 000–37 000 cm^{-1}).

Combined analysis of the ESR and UV–vis DR spectra led us to a conclusion [46,47] that before the vacuum heat treatment copper in Cu-ZSM-5 zeolites exists not only as isolated Cu^{2+} ions but also as $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$ chains stabilized inside the zeolite channels by water molecules. In

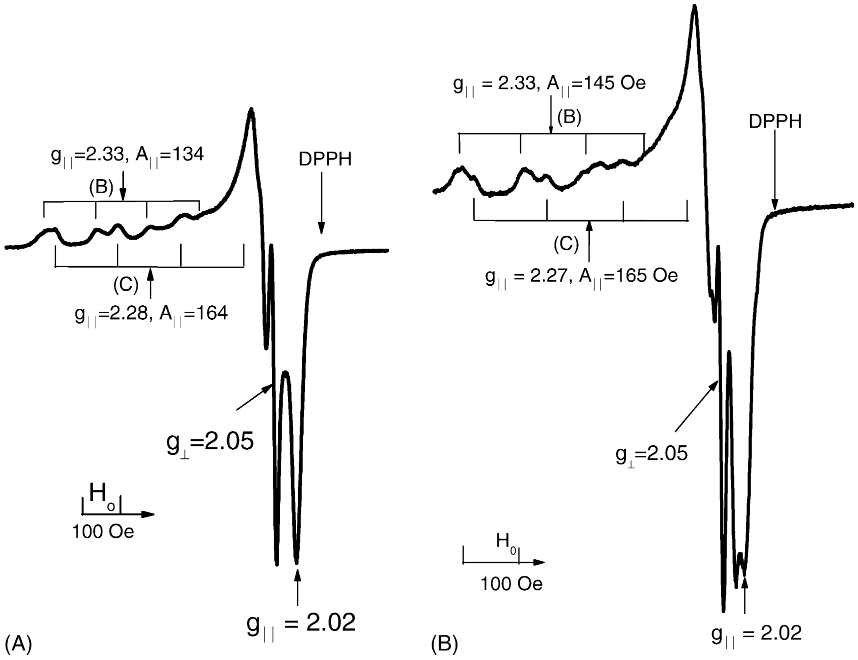

Fig. 4. Typical ESR spectra (77 K) of calcined Cu-ZSM-5 catalysts after vacuum heat treatment at 400 °C for 3 h. (A) 1.26%Cu-ZSM-5-30-75 (sample 7, Table 2), (B) 2.75%Cu-ZSM-5-17-108 (sample 2, Table 2).

this case, the ESR spectrum may not be observed due to a strong exchange interaction between the Cu^{2+} ions in these chains. Note that the probability of the strong exchange interaction between the copper ions in the chain is especially high for d_z^2 ground state of the copper ions. Stabilization of the latter can be facilitated by the arrangement of the copper ions into chains. Heat treatment under vacuum results in the removal of water molecules coordinated to the copper ions in the chain-like structures. This increases the covalence of the copper–oxygen bonds in the chains, which can lead to localization of the unpaired electron on the oxygen atom. Such changes in the electronic structure of copper are observed in the UV–vis DR spectra as a CTLM transition at 18 000–23 000 cm^{-1} [47,48] (Fig. 6). In addition, the heat treatment under vacuum leads to partial "internal" reduction [60] of the copper ions in the chains with the formation of $\cdots O^{-}\cdots Cu^{+}\cdots O^{-}\cdots Cu^{+}\cdots O^{-}\cdots$ chains. It appears that they are observed in the ESR spectra as O^{-} anion radicals with $g_{\parallel} = 2.02$ and $g_{\perp} = 2.05$ [46,48] together with the signals of isolated Cu^{2+} ions (Fig. 4).

The chain structures are formed due to participation of polynuclear copper complexes of variable composition produced upon hydrolysis of the copper salt during the ion exchange with the proton of H-ZSM-5 zeolite, or due to hydrolysis of $[Cu(H_2O)_6]^{2+}$ ions localized in the cation exchange positions of the zeolite during the ion exchange and catalyst washing stages. The stabilization of chain-like copper-oxide structures is possible due to ordered ZSM-5 channels and their size (~0.54 nm × 0.56 nm).

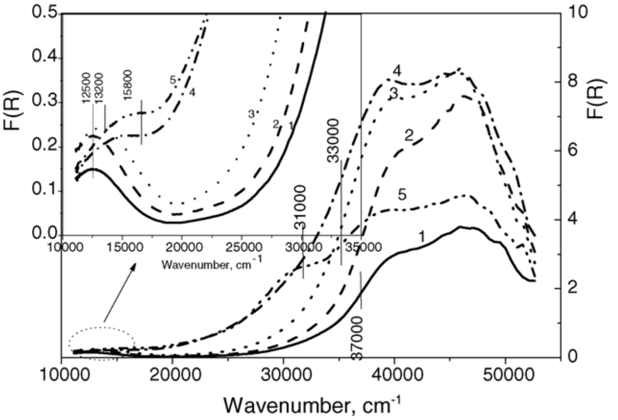

Fig. 5. UV–vis DR spectra of 2.27%Cu-ZSM-5-30-135 (sample 8, Table 2) after different vacuum heat treatments. (1) Initial sample; (2) after treatment at 25 °C for 1 h; (3) after treatment at 150 °C for 1 h; (4) after treatment at 300 °C for 1 h; (5) after treatment at 400 °C for 4 h.

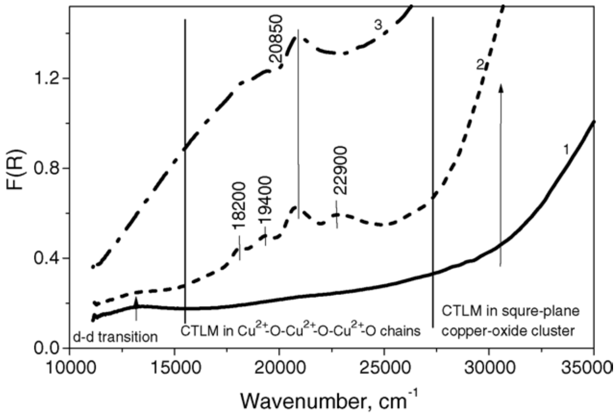

Fig. 6. UV–vis DR spectra of 1.54%Cu-ZSM-5-30-91 prepared by ion change in aqueous solution of copper nitrate at 80 °C without washing after different vacuum heat treatments. (1) Initial sample; (2) after treatment at 150 °C for 1 h; (3) after treatment at 300 °C for 1 h.

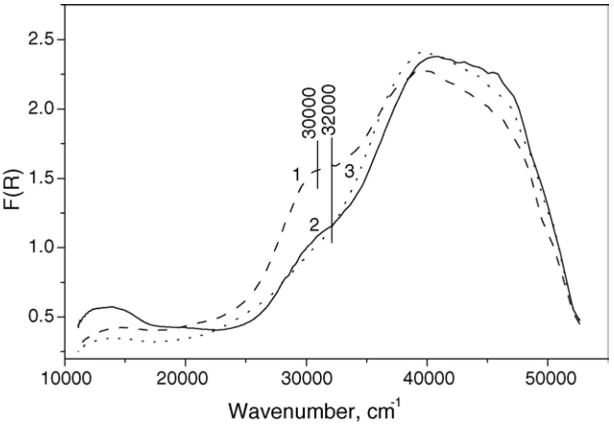

Fig. 7. UV–vis DR spectra of 1.88%Cu-ZSM-5-17-74 (sample 1, Table 2) evacuated at 400 °C for 4 h (curve 1) and for 16 h (curve 2) and 1.2%Cu-ZSM-5-45–102 (sample 19, Table 2) evacuated at 400 °C for 4 h (curve 3).

3.5. Identification of chain-like copper-oxide structures

3.5.1. A.b. at 18 000–23 000 cm^{-1} in UV–vis spectra

While the nature of bands in the d–d transition region [57] and the UV region at 30 000–32 000 cm^{-1} is well known [57], the bands at 18 000–23 000 cm^{-1} need to be assigned. The absorption bands at 18 000–23 000 cm^{-1} are observed only when Cu-ZSM-5-30 catalysts are prepared under conditions that facilitate hydrolysis, namely, by ion-exchange with copper acetate solution at pH ~6 or with copper nitrate solution at elevated temperatures [48]. The analysis of d–d transitions for various copper compounds with coordination number ≥ 4 [57,61] proves that for oxide ligands the energy of these transitions can never reach even 15 000 cm^{-1}. On the other hand, the shift of the CTLM transitions of copper oxide structures with c.n. ≥ 4 (e.g. the band at 30 000–32 000 cm^{-1} [57]) into this region does not seem to be likely either because it requires high covalence of the copper–ligand bond. Most likely, these are CTLM transitions in low-coordinated linear copper clusters with c.n. = 2.

This assignment is in a good agreement with the parameters of the electronic spectra of linear $CuCl_2$ molecules [62]. For the latter, the d–d transitions are observed in the low-frequency region ($\nu_1 = 5000$ and $\nu_2 = 9000$ cm^{-1}), while CTLM is a wide band around 19 000 cm^{-1} [62].

This assignment is proven by quantum chemical calculations performed at the unrestricted DFT level [47]. The calculations of the low-energy electronic transitions for $Cu(OH)_2$ molecule have shown [47] that the charge transfer takes place at 16 000–20 000 cm^{-1}, irrespective of the molecule symmetry (D_∞ and C_{2h}). The criteria for assigning the transitions to d–d or CTLM are changes in the charge (q_{Cu}) and spin-density (ρ_{Cu}) distribution. The d–d transitions are accompanied by a noticeable increase in the positive charge and spin-density on the copper atom ($q_{Cu} = 0.99$, $\rho_{Cu} = 0.9$ [47]). The charge transfer results in the opposite change, so that the spin density nearly disappears ($q_{Cu} = 0.54$, $\rho_{Cu} = -0.01$, nearly pure "Cu^+ state" [47]).

3.5.2. ESR spectrum with parameters $g_\parallel = 2.02$ and $g_\perp = 2.05$

The ESR spectrum discerned in the spectra of evacuated Cu-ZSM-5 samples is characterized by axial anisotropy ($g_\perp = 2.05$, $g_\parallel = 2.02$), and the lack of HFS caused by copper isotopes ^{63}Cu and ^{65}Cu [46]. The spectrum width is temperature-independent (77 and 300 K). This spectrum, while ill-defined, was earlier reported in [11,14,16] and assigned to $g_\perp$ of two remaining isolated Cu^{2+} ions with $g_\parallel = 2.30$ (square pyramidal) and $g_\parallel = .27$ (square-plane) [14,16].

The lack of HFS from copper isotopes and deviation of $g_\parallel$ and $g_\perp$ from the values typical for d_z^2-ground state of isolated Cu^{2+} ions ($g_\parallel \sim g_e$, $g_\perp \sim 2.15 \div 2.2$) preclude assignment of the ESR spectrum with $g_\perp = 2.05$ and $g_\parallel = 2.02$ to isolated Cu^{2+} ions stabilized in the octahedral coordination with tetragonal contraction. The lack of HFS from copper isotopes also excludes its assignment to extra additional adsorption of Cu^{2+} ions.

The ESR spectrum with $g_\perp = 2.05$ and $g_\parallel = 2.02$ has been supposed to arise from the formation of hole centers of O^- anions stabilized as σ-form at Cu^+ ions (p^5 and d^{10} electronic configuration, respectively). If an O^- radical anion is stabilized on a cation in σ-form, it is well known that the unpaired electron is localized in the p_z-orbital directed to the cation. As a result, the observed ESR spectrum has axial g-factor anisotropy with $g_\parallel$ close to g_e and no relaxation effects due to degeneracy of the p-orbitals. The $g_\perp$ value therein depends on the charge of the stabilizing cation and changes from 2.07 ($Z = +1$) to 2.02 ($Z = +5/+6$). A deviation of $g_\parallel$ value, which is equal to 2.02 in the ESR spectrum of evacuated Cu-ZSM-5, from g_e ($g_e = 2.0023$) is caused by the contribution of the copper spin-orbit coupling constant (λ^{Cu}). This is possible due to the transfer of the unpaired electron from O^- to Cu^+ upon the formation of a covalent bond between O^- and Cu^+ in $[Cu^+O^-]$ complex. In this case, copper acts as a ligand with respect to paramagnetic O^- ion, and the contribution of λ^{Cu} to $g_\parallel$ value will be significant, especially for O^- radical anions in σ-form. The absence of the copper HFS, which would be observed as coupling of the unpaired electron of the O^- radical anion with the nuclear magnetic moments of copper isotopes ($I = 3/2$), is an evidence of a strong exchange interaction between O^- radical anions in the chain.

This assignment is proven by quantum chemical calculations performed at the unrestricted DFT (density functional theory) level within the ADF package using LDA functional [47]. The calculations have shown that the energies of the oxygen p-orbitals and the copper d-orbitals are close in the structures with low coordination number of copper and oxygen with the formal oxidation states $[Cu^{2+}O^{2-}]$, e.g., in CuO and $Cu(OH)_2$ molecules. As a result, pd-mixing of the oxygen and copper orbitals facilitating internal self-reduction is possible [60]. For example, DFT calculations of CuO and $Cu(OH)_2$ molecules have shown the ground state to have the electronic structures corresponding to Cu^+. These states are lower in energy than the state corresponding to Cu^{2+} by 1.1 and 1.5 eV, respectively. If CuO or $Cu(OH)_2$ molecule interacts with two water molecules at a Cu–OH_2 distance of 2.05 Å, the ground state of both systems is the one corresponding to Cu^{2+} [46]. In other words, internal self-reduction and self-reoxidation: $Cu^{2+} + O^{2-} \Leftrightarrow Cu^+ + O^-$, is inherent for CuO molecules during dehydration and hydration.

3.5.3. A.b. at 15 000–17 000 cm^{-1} in the UV–vis spectra

There are two distinguishing features in the UV–vis DR spectra of evacuated Cu-ZSM-5 samples prepared from ammonia copper acetate solution with high copper contents (>2 wt.%). First, an absorption band at 15 000–17 000 cm^{-1} was observed in the spectra of Cu-ZSM-5-30 and Cu-ZSM-5-45 evacuated at 300 and 400 °C (Fig. 5, curves 4 and 5), while a wide absorption band at 22 500 cm^{-1} was observed in the spectrum of Cu-ZSM-5-17. Second, the band at 22 500 cm^{-1} was very weak in the spectra of all Cu-ZSM-5 evacuated at 400 °C for 20 h.

The nature of the bands at 15 000–17 000 and 22 500 cm^{-1} was still not clear. In order to ascertain it, it is important to note that these bands are characterized by very high extinction. We suppose that the bands at 15 000–17 000 and 22 500 cm^{-1} should be assigned to $Cu^{2+}\cdots Cu^+$ intervalence transitions. Based on physical principles [57], the energies of intervalence transitions and, consequently, their positions in the UV–vis DR spectra are determined by the difference of the energies of ground (g) and excited (e) states ($E_{IV} = W_e - W_g$ [57]), for example, a pair $Cu^{2+}\cdots Cu^+ \leftrightarrow Cu^+\cdots Cu^{2+}$. Therefore, these transitions can be observed anywhere from the IR to the UV region of the spectrum. This assignment is in a good agreement with the band at 17 000 cm^{-1} observed earlier in the UV–vis DR spectra of high-temperature Cu–Zn–Al oxide catalysts for methanol synthesis [63]. From physical considerations, $Cu^{2+}\cdots Cu^+$ intervalence transitions can characterize mixed-valence Cu^{2+}–Cu^+ pairs in close proximity, e.g. ELO-bridged dimers (Cu^+–O–Cu^{2+}) [27] or partially reduced copper-oxide clusters $Cu^+/(Cu^{2+}O)$ [64]. The former have been proposed to be characterized by CTLM at 22 700 cm^{-1} in the UV–vis spectra of Cu-ZSM-5 observed after exposure to oxygen at 500 °C [27]. The existence of the latter is assumed from the FTIR spectra of adsorbed CO as an absorption band at 2137 cm^{-1} [64]. There are two possible reasons for observation of $Cu^{2+}\cdots Cu^+$ intervalence transitions in the UV–vis spectra of Cu-ZSM-5 samples.

First, such pairs of Cu^{2+} and Cu^+ ions located close to each other are likely to result from partial reduction of copper cations in $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$ chains. This suggestion is supported by analogy with reduction of strong magnetic associates Cu^{2+}–O–Cu^{2+} in Cu–Y zeolites after vacuum heat treatment [65] and in Cu–Zn–Al oxide catalyst after heating in hydrogen at 350 °C or calcination in air at high temperature [65].

Second, ammonia molecules remaining in the coordination sphere of Cu^{2+} ions even after calcination of Cu-ZSM-5 catalysts facilitate the reduction of Cu^{2+} ions to Cu^+ during the vacuum heat treatment. Such reduction can also result in the appearance of a $Cu^{2+}\cdots Cu^+$ intervalence transition for adjacent copper ions. Similar reduction of Cu^{2+} ions to Cu^+ has been earlier observed during calcination of CuY zeolites with preadsorbed NH_3 [59] and with NH_3 introduced during preparation at pH ~10 [65].

The above assumptions appear to explain the main features of the ESR and UV–vis spectra of evacuated Cu-ZSM-5 samples. These features can be used for identification of chain-like copper-oxide structures with different electronic state of copper ions. Oxidized structures, $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$, in which some Cu^{2+} ions are stabilized in d_z^2-ground state, are formed during dehydration and characterized by a CTLM band at 18 000–23 000 cm^{-1}. Reduced structures, $\cdots O^-\cdots Cu^+\cdots O^-\cdots Cu^+\cdots O^-\cdots$, resulting from self-reduction are observed by the ESR spectra with parameters corresponding to O^- radical anions ($g_{\|} = 2.02$ and $g_{\perp} = 2.05$). Structures with mixed-valence copper ions, Cu^{2+} and Cu^+, are observed in the UV–vis DR spectra as $Cu^{2+}\cdots Cu^+$ intervalence transition bands around 15 000–17 000 and 22 500 cm^{-1}. Thus, –(Cu–O–Cu)– fragments with ELO are proven to be present in Cu-ZSM-5. However, the ESR and UV–vis DR studies do not give information on the exact number of copper ions in the chain-like copper-oxide structures. Similar to water solutions, the number of Cu ions is supposed not to exceed 3–4.

3.6. Comparison of the electronic state of Cu^{2+} ions and catalytic activity of Cu-ZSM-5

For each series of the catalysts, the specific catalytic activity remains constant at Cu/Al ≤75–80% and goes down when the exchange level is increased beyond this value. When catalysts with the same Cu/Al ratio and different Si/Al ratios are compared, the specific catalytic activity goes down with the zeolite Si/Al ratio decrease (Fig. 2C). The features of the catalytic activity of Cu-ZSM-5 samples with different Cu/Al ratios indicate that part of copper ions are inactive in NO SCR by C_3H_8.

Using ESR and UV–vis DR, it has been found that in the samples with Cu/Al <50% most copper ions are located in cation-exchange positions of the zeolite in the form of isolated Cu^{2+} ions ($g_{\|} = 2.38$, $A_{\|} = 130$ G, $g_{\perp} = 2.08$; $\Delta(T_{2g} - E_g) = 12\,500$ cm^{-1}). Their formation is promoted by the use of aqueous copper nitrate solutions (0.0125–0.4 M), ammonia copper acetate solutions (≤0.0125 M) and zeolites with low Si/Al ratio (~17). Isolated Cu^{2+} ions are stable with respect to reduction in vacuum.

Square-plain copper oxide clusters (CTB L → M 30 000–32 000 cm^{-1}) localized on the zeolite surface have been found to predominate in the samples with Cu/Al ≥140%. Their formation is promoted by the use of ammonia copper acetate solutions (pH ~10) and zeolites with high silicate modulus (Si/Al ≥30). They are formed due to decomposition of copper polyoxoaminocomplexes and $Cu(OH)_2$ resulting from hydrolysis of copper tetraammoniate during the ion exchange.

The maximum concentration of chain-like copper-oxide structures stabilized in the ZSM-5 channels is, most likely, observed in the samples with Cu/Al ratio between 75 and 100%. They are formed most efficiently when copper acetate solutions with pH ≥5.5 are used for the synthesis. After dehydration during the thermal treatment they can be stabilized in the oxidized (–Cu^{2+}–O^{2-}–Cu^{2+}–O^{2-}, CTB L → M 18 000–23 000 cm^{-1}), reduced (–Cu^{+}–O^{-}–Cu^{+}–O^{-}, $g_{||} = 2.02$, $g_{\perp} = 2.05$) or mixed valence states (–Cu^{2+}–O^{2-}–Cu^{+}–O^{-}, IVT $Cu^{2+} \rightarrow Cu^{+}$ 15 000–17 000 cm^{-1}). The above signals can be used for identification of the chain structures.

Comparison of the data on the specific catalytic activity of Cu-ZSM-5 samples (Fig. 2C) and the copper electronic states indicates that the catalytic activity decreases when most copper is stabilized in the square-plain copper oxide clusters (Cu/Al > 140%). The assumption of the low catalytic activity of the square-plain clusters is also confirmed by the data on the activity of Cu-ZSM-5 samples with Cu/Al > 200% with part of copper, most likely, isolated Cu^{2+} ions and chain structures, washed out by the ion exchange using an ammonium chloride solution. After removal of this part of copper from the catalyst, the NO conversion decreases, especially at temperatures below 400 °C (Table 3). The specific catalytic activities of re-exchanged Cu-ZSM-5 samples prepared from ammonia copper acetate solution are close to those of the initial samples with Cu/Al > 200% (N4-6, Table 3), but lower than the activities of the initial samples with similar copper contents prepared from aqueous and ammonia copper acetate solutions (N14, Table 2).

Therefore, the activity increase can be correlated with the growth in the number of isolated Cu^{2+} ions and/or chain copper oxide structures in the Cu-ZSM-5 samples. The ability of copper ions for reduction and reoxidation in the chain structures allows us to conclude that their participation in the catalytic NO SCR by C_3H_8 is more preferable.

4. Conclusions

The effect of ion exchange conditions, such as the Si/Al ratio, precursor copper salt, pH and concentration of solution, on the catalytic activity of Cu-ZSM-5 in SCR NO by propane and on the electronic states of copper ions has been studied. The use of aqueous copper acetate solution with pH ~6 has been found to be preferable because this solution allows for preparation of Cu-ZSM-5 catalysts with Cu/Al ~100% using lower concentration (4–8 mg/ml) than the aqueous solutions of other copper salts (nitrate, sulfate or chloride). In this case, the NO conversion in NO SCR by C_3H_8 has been found to reach a maximum value at Cu/Al ratio about 75–100% and remain constant at higher Cu/Al, irrespective of the Si/Al ratio. Lowering of the copper acetate solution pH by adding nitric, sulphuric or hydrochloric acid leads to a decrease of the Cu-ZSM-5 activity, whereas the copper content and the Cu/Al ratio in the Cu-ZSM-5 samples are not changed.

In addition to isolated Cu^{2+} ions in distorted octahedral coordination (ESR: $g_{||} = 2.39$, $g_{\perp} = 2.08$, $A_{||} = 130$ G; UV–vis DR: $\Delta(T_{2g} - E_g) = 12\,500$ cm^{-1}) and square-plain copper oxide clusters (30 000–32 000 cm^{-1}), Cu-ZSM-5 catalysts calcined in air at 500 °C have been assumed to contain $\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots Cu^{2+}\cdots O^{2-}\cdots$ chain-like structures stabilized inside the zeolite channels. These chain-like copper-oxide structures can be identified by a distinctive CTLM band at 18 000–23 000 cm^{-1} in the UV–vis DR spectra. The maximum concentration of the chain-like copper-oxide structures is likely to be found in the samples with the Cu/Al ratios between 75 and 100%.

The chain structures are easily reduced and reoxidized. They are even capable of self-reduction. These transformations of copper ions are accompanied by the appearance of an ESR signal with parameters corresponding to O^{-} radical anions ($g_{||} = 2.02$ and $g_{\perp} = 2.05$) and Cu^{2+}–Cu^{+} intervalence transitions (15 000–17 000 cm^{-1}) in the UV–vis DR spectra. These species may be responsible for the catalytic activity of Cu-ZSM-5 catalysts.

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