Redox Behavior of High Si/Al Ratio Cu–ZSM5 in NO Decomposition[1]

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Abstract—Commercial H–ZSM5 zeolites with a Si/Al ratio equal to 25 and 75 have been exchanged using copper acetate aqueous solutions with different concentrations. Copper saturation is reached at the 130 and 230% level of Cu exchange for Si/Al equal to 25 and 75, respectively, although FTIR spectra showed that a fraction of Al–OH exchange positions is still available. Catalytic activity experiments of NO decomposition have been carried out at 450°C in a fixed bed reactor. Catalysts have been characterized with H_2 TPR and NO adsorption experiments at 120°C. All samples are partially reduced upon thermal treatment under inert flow (He) leading to the formation of Cu^+-containing sites in addition to a fraction of differently reduced copper species. The Cu^+-containing sites, also responsible for NO adsorption and subsequent production of N_2O at 120°C, have been proposed to be the active centers. A quantitative estimation of these species, likely having multi-ionic structure, has been provided.

1. INTRODUCTION

The catalytic decomposition of NO into N_2 and O_2 represents an attractive way to remove nitrogen oxides from combustion flue gases since no addition of a reducing agent is required [1]. Cu–ZSM5 is the most promising catalyst, and, although several limitations hinder practical applications, it has been the object of a lot of investigations to understand the unique behavior of ZSM5-exchanged copper [1–4]. In particular, the activity of Cu–ZSM5 has been associated with the capacity to desorb oxygen at high temperature, also in the absence of a reducing reactant, related to the spontaneous self-reduction of copper (II) [4, 5]. It is generally accepted that this phenomenon generates the active sites for NO decomposition. Valyon and Hall [6] proposed that desorption of ELO (Extra Lattice Oxygen) atoms is mainly responsible for Cu self-reduction, but they did not exclude the participation of lattice oxygen as well. In order to explain the emission of water detected by Iwamoto et al. [3] during the reduction, the formation of reduced centers was attributed to the dimerization or oligomerization of copper species, as $[CuOH]^+$, which can be dehydrated giving rise to Cu^+ chains connected through oxygen atoms [7, 8]. Cu speciation for Cu–ZSM5 with different Cu content and a Si/Al ratio about 14 was determined by Da Costa et al. [9] who found both isolated Cu^{2+} monomers and Cu^{2+} dimers, the fraction of the latter being increased by increasing copper content, whereas no CuO was

detected. The amount of monomers, quite constant in all samples, was associated with the number of couples of Al sites sufficiently close to each other to bind a Cu^{2+} ion. With increasing the Cu/Al ratio, the average Cu–Cu distance decreases leading to the formation of dimers-type species, proposed as the cationic species exchanged in the zeolite and characterized by the formation of Cu–O–Cu bridges with high oxygen lability.

Concerning the catalyst ability in the decomposition of NO, it has been observed that the TOF (turnover frequency) of the reaction increases with the copper loading [6, 10] suggesting that more active species can be formed approaching high exchange levels. Formation of N_2 should occur provided that two NO molecules are close enough to react [11]. On the other hand, oxygen release, generating Cu^+ active sites, also requires the proximity of at least two copper sites, as in the redox reaction mechanism proposed by Pirone et al. [12]. For this reason, Iwamoto et al. [3] firstly proposed a redox mechanism involving the presence of two reduced copper sites in very close proximity. Nevertheless, since the probability to have two sufficiently close copper sites in ZSM5 with a high Si/Al ratio is very poor, many authors exclude that active centers could be associated with single-site copper exchanged species. Moden et al. [13, 14] reported that the number of dimeric centers with labile oxygen atoms is proportional to the rate of N_2 formation from NO. Dimeric Cu(I) species were proposed to be responsible for NO decomposition also by Moretti el al. [15] who found a constant value of TOF, independent of both copper loading and the Si/Al

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[1] This article was submitted by the authors in English.

ratio, when calculated on the basis of copper titrated by irreversible N_2 adsorption at low temperature. O-bridged Cu pairs were suggested by Goodman et al. [16] by theoretical calculations.

On the basis of the considerations reported in the literature, copper self-reduction seems the fundamental feature providing catalytic activity in NO decomposition to N_2. Nevertheless, the question still unanswered is if all copper species able to spontaneously desorb oxygen at high temperature are able to activate the redox mechanism of NO decomposition as well.

In this paper a qualitative and quantitative analysis of active copper species has been performed by investigating the redox behavior of over-exchanged Cu–ZSM5 catalysts with high Si/Al ratios, i.e., with a quite low concentration of potentially exchangeable Al positions. A Cu–ZSM5 with Si/Al = 500 (approaching the silicalite composition) and a CuO/SiO_2 sample were also studied in order to compare the redox properties of copper exchanged on zeolite defects or not exchanged at all. The main features of copper species providing the catalytic activity in NO decomposition were determined.

2. EXPERIMENTAL

2.1. Preparation of Catalysts

The Cu–ZSM5 samples were prepared by ion-exchange of a commercial H–ZSM5 zeolite (Zeolyst CBU–5020, Si/Al = 25, 75) with BET specific surface area in the range 250–400 m^2/g in aqueous solution of copper(II) acetate monohydrate (Aldrich purity 99.8%) at 50°C for 2 h. The concentration of copper in solution ranged from 0.8 to 100 mM for ZSM5 with 25 and 75 Si/Al ratio. A 20 mM copper acetate solution was used to exchange a silicalite-like zeolite (Si/Al = 500), used for comparison. Due to the high copper ion/zeolite amount ratio in all preparations, the pH variation during the exchange procedure was always lower than 10% of the initial value. After the exchange the sample was centrifuged, washed twice with bidistilled water, and dried at 120°C overnight. Finally, the catalyst was calcined according to the following procedure: (a) 2 h at 550°C (heating 9 K/min) under helium flow; (b) cooling down to room temperature; and (c) 2 h at 550°C (heating 9 K/min) under 1% O_2/He mixture flow.

A silica-supported copper oxide (0.93 wt %) catalyst, also used as reference material, was prepared by wet impregnation with copper acetate and calcined as the exchanged zeolites were.

2.2. Catalytic Activity Tests

The catalytic tests were carried out in a fixed-bed microreactor consisting of a quartz tube (I.D. 1.0 cm) with a porous disk supporting the catalyst particles (Φ = 200–400 μm) heated by an electrical furnace (LENTON) with three heated and temperature-controlled zones. The temperature of the catalytic bed was measured by a Chromel-Alumel thermocouple, placed in another quartz tube, coaxial and internal to the reactor. Flow rates of 1% NO/He (NO_2 impurity about 150 ppm) and pure He (99.995%) were measured and controlled by mass flow controllers (BROOKS 5850S). Before each experiment, the catalyst was treated in He flow (30 l/h) for 2 h at 550°C in order to reduce Cu^{2+} to Cu^+ [5, 7, 15, 17, 18]. The inlet and the outlet gas streams were analyzed by Hartmann and Braun continuous analyzers for NO, N_2O (URAS 10 E), and O_2 (MAGNOS 6G), while the NO_2 concentration was indirectly evaluated through a NO_2-to-NO catalytic converter (Hartmann and Braun CGO-K). The measurement of catalytic activity in NO decomposition was carried out at 450°C by feeding 5000 ppm of NO in He, with a contact time ranging from 0.08 to 0.2 g s cm^{-3} chosen at a suitable value so to operate at a NO conversion to N_2 low enough (<15% in all experiments) to assume a differential reactor behavior.

The catalytic performances were expressed as reaction rate w (NO moles converted to N_2 per second and per gram of catalyst) or as turnover frequency TOF (NO molecules converted to N_2 per second and per copper atom) in order to compare samples with different copper contents.

2.3. Catalyst Characterization

Cu content was determined using a Hach Drel 2000 UV-VIS spectrophotometer at 560 nm after dissolving the zeolite in HF aqueous solution, and the corresponding exchange level was evaluated according to the equations reported in [19] suitably modified for each Si/Al ratio.

The zeolite catalysts will be indicated with the following code: Cu–Z-x–y, where x represents the Si/Al ratio of the parent zeolite and y the exchange level.

XRD measurements were performed using a PW 1100 Philips XRD diffractometer with CuK_α radiation from $2\theta = 5°$ to 40°.

BET surface areas were measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorptomatic.

FTIR spectra were recorded at 550°C with a Perkin-Elmer Spectrum GX spectrometer with a spectral resolution of 4 cm^{-1} on the catalyst pressed into a self-supported disk outgassed at the same temperature for 1 h in an IR cell equipped with a ZnSe window.

NO adsorption experiments were carried out at 120°C with a 600 ppm NO/He gas mixture (20 l h^{-1}) using the same experimental apparatus described for the catalytic tests. After the adsorption of NO, the reactor was purged with He flow, and then, a TPD experiment was carried out by heating 9 K/min up to 550°C in flowing He.

The H_2 TPR experiments were performed in the same reactor used for catalytic tests feeding a 2% H_2/N_2 high purity mixture. The inlet and the outlet H_2 concen-
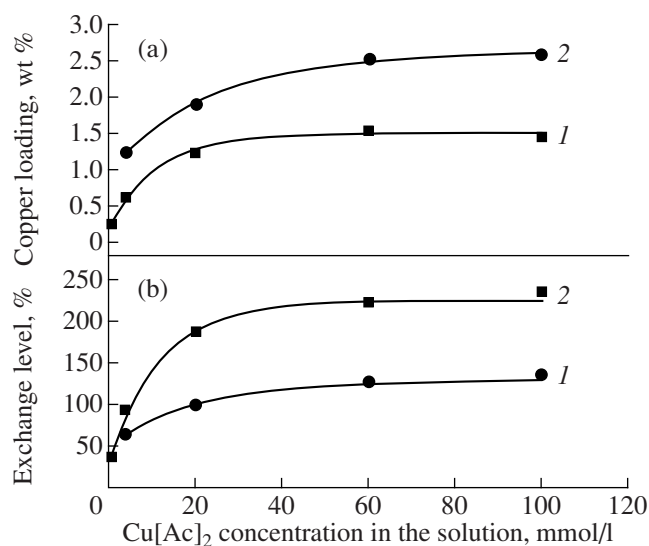
Fig. 1. Copper loading (a) and exchange level (b) as a function of Cu[Ac]$_2$ concentration in the solution for ZSM5 with Si/Al = 25 (*1*) and Si/Al = 75 (*2*). (Exchange time = 120 min, exchange temperature = 50°C).

Fig. 2. FTIR spectra in the region 3000–4000 cm^{-1} for Z-25 (*a*, Z-25; *b*, Z-25–100; *c*, Z-25–136) and Z-75 (*a*, Z-75; *b*, Z-75–188; *c*, Z-75–237) recorded at 550°C under vacuum.
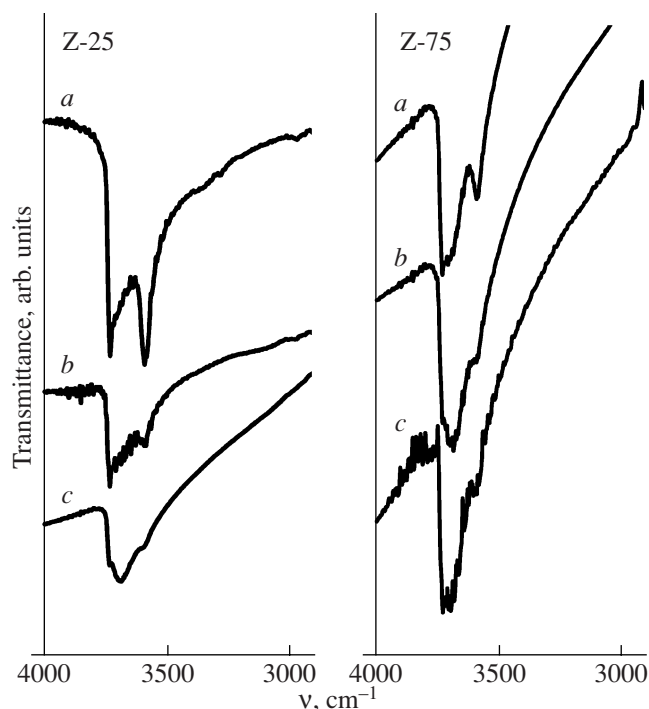
tration was monitored by a Rosemount NGA2000 continuous analyzer. Water possibly produced during the TPR was kept with a CaCl$_2$ trap. A different amount of catalyst, depending on the Cu content in the sample, was used. Two different pretreatments were effected for each sample: (i) He flow (30 l h^{-1}) for 2 h at 550°C (pre-reducing treatment) and (ii) pure O$_2$ flow (6 l h^{-1}) C for 15 min at 150°C (preoxidizing treatment).

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

XRD analysis showed that all exchanged samples keep the MFI structure without appreciable loss of crystallinity with respect to the parent H–ZSM5. Moreover, no diffraction peaks corresponding to formation of copper oxides were evidenced in the XRD patterns of zeolites and CuO/SiO$_2$.

The effect of the salt concentration in the solution for catalyst preparation on both the amount of copper loaded and the consequent exchange level is reported in Fig. 1. As expected, due to the higher number of exchangeable positions, higher copper loadings were obtained for the zeolite with Si/Al = 25. Regardless of the Si/Al ratio, the copper loading increases with the Cu^{2+} concentration in the exchange solution up to a limit value corresponding to about 2.7 and 1.3 Cu wt % for the samples with Si/Al = 25 and 75, respectively (Fig. 1a). The limit exchange level reached for both zeolites far exceeds 100% (Fig. 1b) thus suggesting that after the saturation of the exchange positions additional copper is introduced in the zeolite in a different form. Nevertheless, FTIR spectra in the hydroxyl region (Fig. 2) show that the band corresponding to the bridg-

ing OH (at about 3660 cm^{-1}) [20], the exchange sites, although significantly reduced, is still present even for over-exchanged Z-75 (Fig. 2, spectra *2*, *3*), despite the very low amount of exchangeable positions of the parent zeolite and the relatively high copper content. This indicates that the exchange does not take place through an initial saturation of Al positions but that a different exchange mechanism likely occurs. Indeed, a fraction of copper can be exchanged as multi-ionic species as [Cu$_x$O$_y$(OH)$_z$]$^{+(2x-2y-z)}$ giving rise to these high exchange levels even when some Al–OH centers are still available.

3.2. Catalytic Activity Tests

Table 1 reports the results of catalytic activity tests as the rate of NO consumption (*w*) and NO turnover frequency (TOF) evaluated for all samples at 450°C and 5 mbar NO partial pressure.

A negligible activity was observed for both the Cu–Z-500 and the CuO/SiO$_2$ sample, confirming that only copper species exchanged on Al positions of MFI structures are able to decompose NO, while no activity is shown by Cu almost exclusively exchanged on the defects of a ZSM5 zeolite with the same structure (as in the Cu–Z-500). Both for Cu–Z-25 and Cu–Z-75, *w* roughly enhances with increasing the exchange level in the samples. On the contrary, the TOF values are quite scattered, although contained in a quite narrow

Table 1. Rate of NO decomposition expressed as amount of converted NO per unit time and catalyst weight and as TOF (amount of converted NO per unit time and copper atom)

Catalyst	w, (mol NO g^{-1} s^{-1}) $\times 10^7$	TOF, mHz
Cu–Z-25–65	0.47	0.24
Cu–Z-25–100	1.87	0.62
Cu–Z-25–128	1.76	0.46
Cu–Z-25–136	2.25	0.56
Cu–Z-75–94	0.47	0.48
Cu–Z-75–188	0.65	0.33
Cu–Z-75–223	0.68	0.30
Cu–Z-75–237	0.94	0.38

range. The average values, evaluated for each Si/Al ratio, are quite similar suggesting that the copper species present in the over-exchanged ZSM5 show a close value of intrinsic activity, not or weakly depending on the Si/Al ratio.

3.3. TPR Results

TPR profiles of some catalysts, chosen as representative among those investigated, are reported in Fig. 3, for both prereduced and preoxidized samples. The H_2/Cu ratio values, measured by the integration of the area of the TPR signals, are reported in Table 2. The value of this ratio for the preoxidized samples, very close to 1, suggests that copper is mainly present as Cu^{2+} in the starting materials. Two quite well defined peaks were observed for all preoxidized Cu–Z-25 and Cu–Z-75 catalysts, in contrast to Cu–Z-500–952 and CuO/SiO_2 basically showing a single signal with a very small shoulder at about 120 and 280°C, respectively (Fig. 3a). For both Cu–Z-25 and Cu–Z-75 the low tem-

perature signal is peaked at about 250°C, whereas the high temperature signal, appearing at 380°C for Z-25 catalysts, is shifted at about 500°C for Cu–Z-75 zeolites. The relative intensity of the signal at lower temperature, with respect to that at high temperature, enhances with increasing the exchange level of all samples. Similar results were also obtained by Torre-Abreu et al. [21] and Bulanek et al. [22] who proposed that the reduction of bulklike copper oxide species can occur in the same range of temperature of the first stage of the double-step reduction of ionic species from Cu^{2+} to Cu^{+} and from Cu^{+} to Cu^0. On the contrary, no bulk CuO formation was detected by Da Costa et al. [9] who evaluated the same area for the two peaks (with a H_2/Cu ratio = 0.5) confirming the reduction sequence $Cu^{2+} \longrightarrow Cu^{+} \longrightarrow Cu^0$.

The position of the single main TPR peak for Cu–Z-500–952 and CuO/SiO_2, compared with that of the first signal of TPR profiles of Cu–Z-25 and Cu–Z-75 samples, confirms that the formation of CuO bulklike species, in addition to exchanged copper, cannot be excluded. In fact, CuO/SiO_2 is supposed to contain only CuO, whereas the Cu–Z-500 sample, having a negligible value of Al exchangeable positions, should contain copper oxide microclusters and/or copper exchanged on the structure defects.

For all samples the H_2 uptake of the prereduced catalyst is lower than that calculated for the corresponding preoxidized one (Table 2) suggesting that the thermal treatment promotes copper self-reduction notwithstanding the nature of the sample. A significant reduction was observed for both copper silicalite-like zeolite and CuO/SiO_2, thus suggesting that the self-reducing property is not unique to zeolite-exchanged copper, in agreement with other authors who observed the spontaneous reduction of copper oxide films [23] or powder [24] under vacuum. Moreover, this property cannot be easily associable to the catalytic activity, very reducible

Table 2. H_2/Cu ratio (total signal and second peak) evaluated from TPR experiments for both preoxidized and prereduced samples and the N_2O/Cu ratio estimated from NO adsorption experiments

Catalyst	H_2/Cu oxidized, mol mol^{-1}	H_2/Cu reduced, mol mol^{-1}	H_2/Cu 2nd peak, mol mol^{-1}	N_2O/Cu, mol mol^{-1}
Cu–Z-25–65	0.7	0.2	0.07	0.22
Cu–Z-25–100	0.9	0.7	0.34	0.37
Cu–Z-25–128	0.9	0.4	0.30	0.20
Cu–Z-25–136	0.9	0.4	0.27	0.31
Cu–Z-75–94	0.8	n.e.*	0.30	0.22
Cu–Z-75–188	1.0	0.7	0.40	0.16
Cu–Z-75–223	0.8	0.4	0.40	0.29
Cu–Z-75–237	1.0	0.6	0.31	0.20
Cu–Z-500–952	0.7	0.2	–	–
CuO/SiO_2	1.0	0.4	–	–

* Not evaluated due to the small TPR area.

samples being poorly active. Therefore, spontaneous desorption of oxygen at high temperature is not strictly correlated to the generation of copper active sites.

For both Cu–Z-25 and Cu–Z-75 samples, the self-reducing treatment affects only the low temperature signal, the second peak being quite unchanged (Fig. 3b). This could suggest that the pretreatment under inert flow reduces Cu(II) containing species to Cu(I) which are then further reduced to Cu^0 by H$_2$ in the TPR experiment. As a consequence, the fraction of the first peak still present upon prereduction treatment should be associated to not self-reducible copper species. The nature of this copper species has been not investigated; however, the absence of a residual low temperature signal for Cu–Z-25–64 suggests that the formation of these species occurs only when the exchange level approaches or exceeds 100%.

In conclusion, comparative TPR study of oxidized and prereduced Cu–ZSM5 allowed the determination of the redox nature of copper in the zeolite and the quantification of species with different reducibility.

3.4. NO Adsorption Experiments

In some previous papers [12, 25], it was shown that the study of the interaction between NO and copper over-exchanged ZSM5, at temperatures very far from those promoting a steady-state activity in NO decomposition, represented a very good tool to investigate the redox chemistry of these systems. In particular, it was demonstrated that such experiments could be used to titrate copper ions, which are "self-reducible" at high temperature under inert flow or vacuum [3, 7, 8, 15, 17, 18, 21, 26, 27]. The reoxidation of Cu$^+$ sites at low temperature was reported to occur via the transient formation of gaseous N$_2$O during NO adsorption. Due to the supposed redox nature of the NO decomposition mechanism over the Cu–ZSM5 catalyst [1, 3, 7, 27–29], it seems useful to more deeply investigate this property. In particular, the NO adsorption experiments on prereduced catalysts were carried out in order to compare the fraction of self-reducible copper (measured with the TPR analysis) with that which can be subsequently reoxidized by NO.

No formation of N$_2$O was observed for the silicalite-like and CuO/SiO$_2$ samples after catalyst thermal treatment under inert flow, whereas, for the other samples, a transient evolution of N$_2$O was observed during NO adsorption. In Table 2 the results of NO adsorption experiments have been reported as the N$_2$O/Cu ratio. The value of the N$_2$O/Cu ratio changes for the different catalysts and is not associable to the total extent of reduction of each sample evaluated by H$_2$ TPR. Nevertheless, by supposing that the active species contain copper self-reducible to Cu(I), which is responsible for the high temperature TPR peak, the H$_2$ amount corresponding to this signal (Table 2) could be related to the amount of N$_2$O found in NO adsorption experiments,
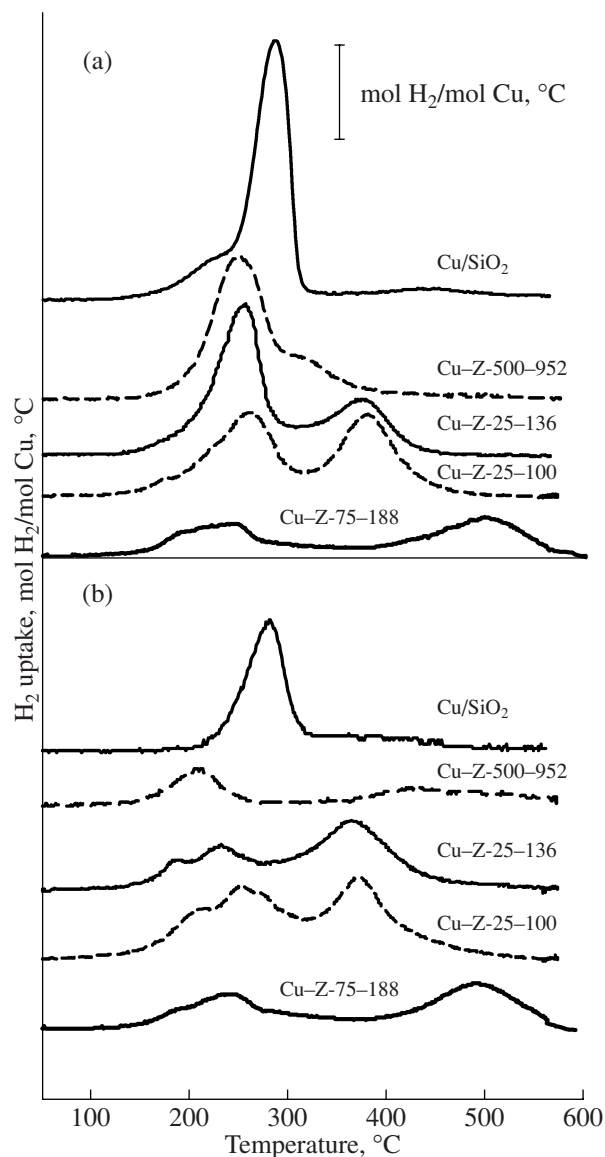

Fig. 3. TPR profiles of some preoxidized (a) and prereduced (b) Cu–Z-25 and Cu–Z-75 catalysts compared with Cu–Z-500–952 and CuO/SiO$_2$.

both normalized to the total Cu content. Except for a few cases, the value of the H$_2$/Cu ratio corresponding to the second TPR peak is very close to the corresponding N$_2$O/Cu ratio suggesting that sites titrated through N$_2$O formation correspond to Cu(II) containing sites reduced to Cu(I) by a pretreatment under inert flow at 550°C. In addition to these species, the thermal pretreatment promotes the reduction of copper with a different nature, likely to metallic copper, which is inactive for NO decomposition. In conclusion, it is reasonable to suppose that only Cu^{2+} exchanged in suitable positions and in a suitable way is able to be self-reduced to Cu$^+$ and reoxidizable by NO producing N$_2$O. Such species are consequently also able to properly decompose NO to N$_2$ in the range of temperatures from

TOF, mHz
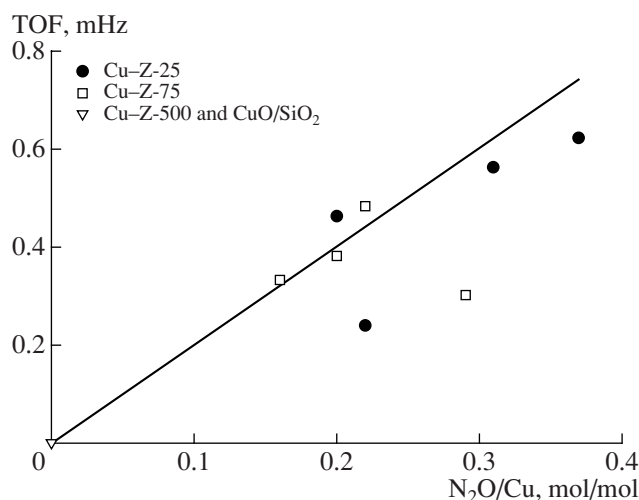
Fig. 4. TOF of NO decomposition as a function of the N_2O/Cu ratio estimated from NO adsorption experiments for the prereduced catalysts.

400 to 550°C [30, 32], since the decomposition of N_2O is very fast under these conditions [31]. All other copper species, even when reducible, are inactive in NO decomposition. As mentioned in the Introduction, the nature of the active species is still debated. In the most recent papers [9, 10], the formation of dimers $\{Cu^{2+}-O^{2-}-Cu^{2+}\}^{2+}$ was asserted by Da Costa et al. [9], coupling H_2 and CO TPR and O_2 TPD techniques, in addition to monomers $\{Cu^{2+}(OH)^-\}^+$ for Cu–ZSM5 with a Si/Al ratio about 14. They also found that the fraction of dimers increased with increasing copper content whereas the amount of monomers was quite constant due to the limited number of Al-sites sufficiently close to each other to bind a Cu^{2+} ion. Moretti et al. [10] also reported that the amount of Cu(I) dimers, detected by N_2 irreversible adsorption, was strictly correlated to the catalytic activity and increases with the exchange level. Due to the high Si/Al ratios of the ZSM5 investigated in this work, the number of close Al-sites is expected to be quite negligible and, as a consequence, the formation of exchanged single copper ions is highly unlikely. As a consequence, considering that the 100% exchange capacity is exceeded for all samples except one, the presence of dimers or even of multicationic species like $[Cu_xO_y(OH)_z]^{+(2x-2y-z)}$ should be supposed in addition to bulk CuO. Moreover, it should be recalled that, as shown by FTIR spectra, some exchange positions are still in their original hydrogen form when the theoretical exchange level of the zeolite far exceeds 100%. This suggests that, for zeolites with high Si/Al ratios, a different exchange mechanism can occur due to the low availability of Al centers, which promotes an easy over-exchange of the ZSM5. The formation of these bi- or multicationic copper species prevails and probably inhibits the complete exchange of protonic Al-sites, probably due to site inaccessibility. Furthermore, the nature of these species can

be assumed to be the same regardless of the Si/Al ratio (25 or 75), since the TOF does not vary too much (Fig. 4). In fact, a significantly lower TOF value should be expected for Cu–Z–75 catalysts, if monomers would be involved in the reaction mechanism, due to the very poor probability to have two exchange positions close enough in a zeolite with such a large Si/Al ratio.

4. CONCLUSIONS

ZSM5 zeolites with a high Si/Al ratio (25 and 75) can easily be over-exchanged with copper. The maximum exchange level, always far exceeding 100%, is reached before saturation of the exchange positions takes place. The increase in the copper load in zeolites, even with a different Si/Al ratio, does not result in a significant difference of TOF, suggesting that active sites having the same nature are preferentially formed in over-exchanged ZSM5 with a high Si/Al ratio. The formation of bi- or multicationic copper species has been supposed to be responsible for the activity. Copper in these species was found self-reducible from Cu(II) to Cu(I) upon thermal treatment generating the active sites for NO decomposition. Additional copper, present in the zeolites as CuO microclusters, although partially self-reducible, is not active for the reaction. The amount of active copper species was estimated by TPR experiments and was found corresponding to the amount of species able to be reoxidized by NO at low temperature producing N_2O. The same species are responsible for NO decomposition at higher temperatures.

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