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Cu ion siting in high silica zeolites. Spectroscopy and redox properties

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Abstract

It has been shown that two main Cu sites present in ion exchanged Cu-ZSM-5 which differ in positive charges on the Cu^{2+} ion, exhibit substantially different redox properties and reactivity towards NO molecules investigated by IR spectra of adsorbed NO and CO, and Cu^{+} emission spectra. The Cu ion with low positive charge (tested by electron density transfer from NO molecule to the cation) is assumed to be balanced by a low negative charge, i.e., a single framework Al atom. This Cu site preferably forms Cu^{+} dinitrosyl complexes and exhibits high stability of Cu^{+} even in oxygen at high temperature (720 K) compared to the other Cu ions with higher positive charges, which are suggested to be balanced by two framework Al atoms. A decisive role of local negative framework charge adjacent to the cation as well as total negative framework charge given by Si/Al ratio for the redox properties and reactivity of the Cu ions has been indicated.

Keywords: Metal ion; Zeolite; Siding; Copper; Cu-ZSM-5; Redox

1. Introduction

Cu loaded high silica zeolites particularly with high Cu/Al loadings have been shown to exhibit unique and stable activity in NO decomposition [1] in contrast to the Cu ions implanted in mordenite, erionite and faujasite zeolite structures. It has been shown that the reaction proceeds via a redox mechanism and monovalent copper is suggested to be responsible for this activity [2]. Formerly, Cu^{+}–Cu^{+} dimeric site [1,3] was considered to be an active center, however, there is not sufficient evidence for such proposal. Lately, a single Cu ion center has been shown to satisfy the reaction mechanism derived from the kinetic studies of NO decomposition [4]. We have developed an experimental approach [5] employing laser induced Cu^{+} photoluminescence spectra, IR spectra of adsorbed NO on Cu^{2+} ions and ESR spectra of Cu^{2+} to identify four different Cu sites in high silica zeolites. Based on the different population of the individual Cu sites depending on the zeolite structural type and composition, both Si/Al and Cu/Al, it has been suggested that two main sites exist in zeolite of MFI structure, the Cu site (denoted in Ref. [5] as Cu-II), which is considered to be balanced by two framework Al atoms, and the Cu site (denoted as Cu-IV) adjacent only to one framework Al (for details, see Ref. [5]). The former Cu site is preferentially occupied at low Cu loadings while the latter site is incorporated in the whole concentration range, but prevails at high Cu loadings, particularly at the exchange level approaching and exceeding stoichiometric exchange ($Cu/Al \geq 0.5$). The Cu site of the type Cu-IV has been indicated as an active site for the reaction of NO decomposition [6].

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This contribution deals with the reducibility–reactivity of the individual Cu sites in MFI structure and shows how it is reflected in redox properties of the Cu ions in Cu-ZSM-5 depending on Cu/Al and Si/Al compositions. IR spectra of NO adsorbed on both Cu^{2+} and Cu^{+} ions and of CO adsorbed exclusively on Cu^{+}, as well as Cu^{+} emission spectra are used to distinguish the redox properties of the individual Cu sites, which are eventually discussed in connection with the Cu-zeolite NO decomposition activity.

2. Experimental

Cu^{2+} loaded ZSM-5 zeolites of various Si/Al ratios were obtained by the ion exchange from Cu acetate and Cu nitrate solutions of the molar concentrations ranging from 0.001 to 0.05 (zeolite compositions see in figures). Redox properties of the Cu^{2+} zeolites were investigated by checking the valence state of the copper on samples oxidized at 720 K for 3 h in 100 Torr of oxygen followed by evacuation at 298 K for 10 min or on samples oxidized and evacuated at 720 K for 3 h. The valence state of copper was determined by IR spectra of adsorbed NO, forming mono- and dinitrosyl complexes of monovalent Cu, and mononitrosyl complexes of divalent Cu, and of spectra of CO adsorbed selectively on Cu^{+} ions (at conditions when mostly monocarbonyls were formed).

Luminescence spectra of Cu-ZSM-5 zeolites, where Cu^{2+} ions were reduced to Cu^{+}, in the range of 350–750 nm were recorded at 298 K employing laser nanosecond kinetic spectrometer (Applied Photophysics) equipped with a $Xe^{+}Cl$ excimer laser using a 20 ns pulse at 308 nm (details in Ref. [3]). All the spectra were monitored at the lifetime of 5 μs. Time resolved FT–IR spectra (Nicolet Magna-550) of the NO adsorption (constant pressure of 40 Torr) or of adsorbed CO (12 Torr) at 298 K (followed by evacuation at 298 K) were recorded on thin transparent plates (approx. 7 mg cm^{-2}). Both spectra exhibited discrete bands which, however, substantially overlapped. The second derivative mode was used to indicate band maxima, and the model Cu-zeolites exhibiting nearly exclusively one band were employed to determine the width of the individual bands before applying spectra deconvolution.

3. Results and discussion

According to the experimental procedure employing Cu^{+} emission spectra and IR spectra of NO adsorbed on Cu^{2+} ions; four different Cu sites with emissions at 450, 480, 510 and 540 nm and corresponding IR vibrations of adsorbed NO at 1921, 1912, 1906 and 1895 cm^{-1}, respectively, were found in the high silica Cu-zeolites. In Cu-ZSM-5 the Cu sites with Cu^{+} emissions at 480 and 540 nm and N–O vibrations at 1912 and 1895 cm^{-1}, respectively, represent the main Cu sites population of which depends on the Cu/Al and Si/Al composition.

As the frequency of N–O IR vibrations of nitrogen oxide adsorbed on the metal ions are a measure of the electron density transfer from the NO molecule to the cation, the Cu site with the band at 1895 cm^{-1} reflects a low electron density transfer from adsorbed NO molecule and thus the Cu site possesses a low positive charge. Therefore, and based on the population of the individual Cu sites on the framework Si/Al ratio [4], this Cu site is assumed to be adjacent to one framework aluminum. On the other hand, the Cu ion with NO vibration at 1912 cm^{-1} possessing a higher positive charge, is suggested to be balanced by two framework Al atoms, "Al pairs" [3] of the structure Al–O–$(Si–O)_n$–Al where we do not specify a value of n. Because of the evidences on the different positive charges on the individual Cu ions we have expected also differences in their redox properties.

When on Cu-ZSM-5 with Cu/Al 0.48 and Si/Al 22.5 (oxidized in 100 Torr of oxygen at 720 K for 3 h followed by evacuation at 298 K for 10 min) was adsorbed NO (40 Torr, 298 K), bands at 1811, and at 1835 and 1775 cm^{-1} corresponding to Cu^{+}–NO and $Cu^{+}(NO)_2$ species, respectively, and a band at about 1910 cm^{-1} reflected Cu^{2+}–NO complexes have appeared similarly as described in [7]. It evidences an important fact that even in Cu-ZSM-5 oxidized in oxygen at high temperature some Cu ions are present in a monovalent state. With increasing adsorption time the bands corresponding to mono- and dinitrosyls of Cu^{+} were transferred into the band (at approx. 1910 cm^{-1}) reflecting $Cu^{2+}NO$ complexes (Fig. 12) and thus oxidation of monovalent to divalent copper. It is clearly seen from Figs. 1 and 2 that in the first stage of the adsorption process the band at 1912 cm^{-1} increases, while next stages are connected with pro-

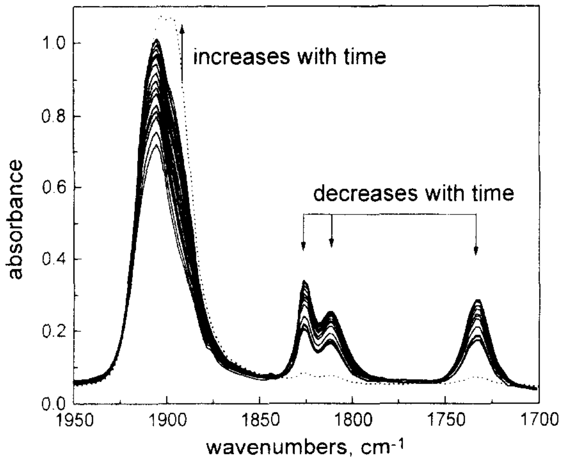

Fig. 1. IR spectra of Cu-ZSM-5 (Si/Al 22.5, Cu/Al 0.48) oxidized by 100 Torr O_2 at 720 K and evacuated at 298 K, after exposition to 40 Torr of NO for up to 130 min (full line) and 20 h (dotted line).

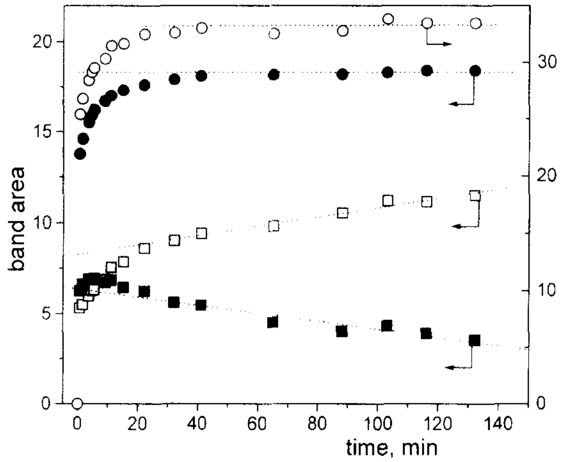

Fig. 2. Time dependence of the individual components of the spectra of Fig. 1. Integral intensity of Cu^+-$(NO)_n$ (■), Cu^{2+}-NO (band at 1895 cm^{-1}) (□), Cu^{2+}-NO (band at 1912 cm^{-1}) (●) and the sum of all Cu^{n+}-$(NO)_n$ species (○).

gressive intensity increase at 1895 cm^{-1}, which results, after a prolonged NO adsorption, in high intensity of the band at 1895 cm^{-1} in addition to the band at 1912 cm^{-1}. Simultaneously, the bands ascribed to Cu^+ mono- and dinitrosyls decrease in intensity. A quantitative analysis of the individual band intensities (band areas after their deconvolution) in dependence on time of NO adsorption is given in Fig. 2. It is shown that the sum of the intensities of the bands corresponding to Cu^{2+}–(NO), Cu^+–(NO) and 0.5 value of the intensity of Cu^+–$(NO)_2$ complexes increases up to the adsorption time of approx. 20 min and then reaches a constant value. Similar time dependence has been obtained for changes in the intensity of the band at 1912 cm^{-1}, while the intensity of the band at 1895 cm^{-1} steadily increases. Up to the adsorption time of 10 min a sharp increase in population of Cu^+ nitrosyl complexes (sum of the intensities of the bands at 1811, 1775 and 1835 cm^{-1}) was observed followed by its steadily decrease above 20 min of adsorption. It indicates that in the first stage of the process (up to approx. 20 min) an adsorption of NO on monovalent and divalent copper is the rate determining step, while when the sum of the intensities attains a constant value the changes in the intensities of the individual bands can be considered as reflecting the oxidation of Cu^+ to Cu^{2+} at individual Cu sites. An opposite trend in the intensity changes at 1895 cm^{-1} (linear increase) to the sum of the intensity of Cu^+ nitrosyl complexes (linear decrease) with constant intensity at 1912 cm^{-1} indicates that the Cu sites which were in a monovalent state in Cu-ZSM-5 and were oxidized by NO are mostly those exhibiting low electron density transfer to the cation and thus low positive charge on the Cu^{2+} ion. Fig. 3 depicts the intensity ratio corresponding to the bands (1775+1835)/1811 cm^{-1} in dependence on the adsorption time. There is a linear decrease of this ratio indicating that preferably Cu^+ dinitrosyls are

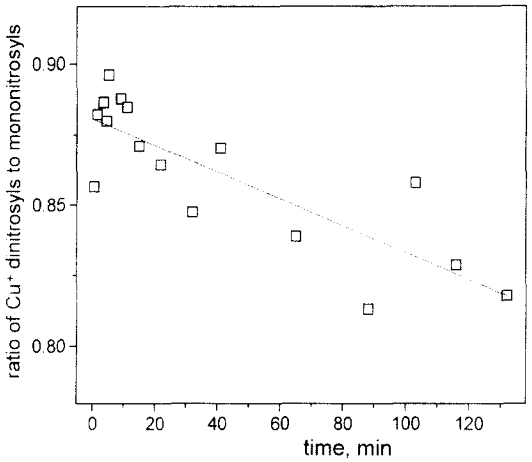

Fig. 3. Change in the ratio of integral intensity of Cu^+–$(NO)_2$ to Cu^+–NO (see Fig. 1) with time of exposition to 40 Torr of NO.

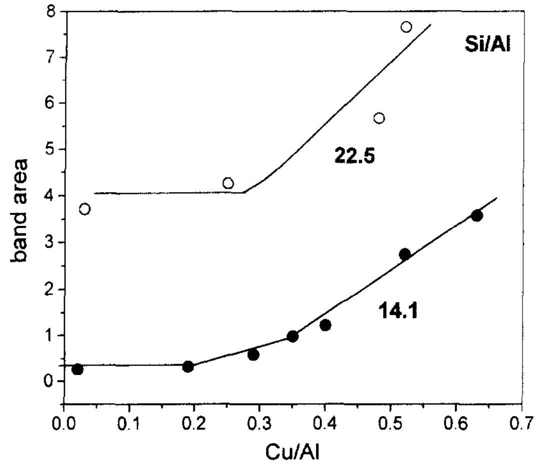

Fig. 4. Cu–CO IR bands integral intensity after CO adsorption on Cu-ZSM-5 (oxidized by 100 Torr O_2 at 720 K and then evacuated at the same temperature) vs. Cu/Al ratio.

oxidized to Cu^{2+}. Moreover, the ratio of intensities of antisymmetrical and symmetrical NO vibrations in dinitrosyls and thus calculated bond angle of two nitrosyls in $Cu^{+}(NO)_2$ complexes was not changed during the adsorption process. It has already been found in [7,8] that on the Cu sites mono- and dinitrosyl complexes are formed, however the data presented here indicate that the Cu^{+} dinitrosyl complexes prevail at one type of the Cu site. This is that one with a low positive charge (reflected in the Cu^{2+}–NO band at 1895 cm^{-1} after zeolite oxidation).

Further evidences on the different reducibility of the Cu sites in ZSM-5 matrix was given from the IR spectra of CO adsorption on Cu-ZSM-5 which is selectively adsorbed only on Cu^{+} (Fig. 4). The Cu zeolites differing in Cu/Al and Si/Al ratios were oxidized (as above) and followed by evacuation at 720 K for 3 h. After that CO was adsorbed at 298 K for 1 h and shortly evacuated thus only monocarbonyl species were detected with the intense IR band with maximum at 2158 cm^{-1}. We have reported [5] that depending on Cu loadings in ZSM-5, at first Cu sites of the type Cu-I (with very low concentration and so not considered here) and Cu-II are occupied and Cu-IV sites prevail at Cu/Al values approaching and/or exceeding equilibrium exchange level. For Cu-ZSM-5 with Si/Al 14.1 low number of Cu ions was detected as Cu^{+} via CO adsorption at low Cu loadings after pretreatment given above. With increasing Cu content in the zeolite the number of Cu^{+} ions substantially increased. When a zeolite with Si/Al ratio of 22.5 was investigated a similar dependence on Cu/Al ratio was observed, but the number of Cu^{2+} ions reduced to Cu^{+} by pretreatment procedure, was substantially higher even at lower loadings. It indicates that the Cu sites (type IV) with a low positive charge are readily reduced and that negative charges adjacent to the Cu site, determined by the presence and distribution of Al in the zeolite framework, play a decisive role for the reduction of the individual divalent Cu ions or for the stability of a monovalent state of Cu ions implanted in zeolite matrix.

From the above results it can be concluded that both the local negative charge adjacent to the Cu ion, given by the distribution of Al in the framework ("Al pair" or single Al atom), and delocalized negative charge given by the total Al content in the framework (Si/Al) control the Cu sites reducibility. From it follows that depending on Cu/Al/Si composition of the zeolite, different Cu^{2+}/Cu^{+} valence ratios are obtained.

Not only a higher reducibility and thus stability of the Cu-IV site in a monovalent state but, as reflected in a higher level of dinitrosyl complexes formation compared to other sites, its higher interaction with respect to NO was monitored also via Cu^{+} emission. Fig. 5 depicts Cu^{+} emission spectrum of the Cu-ZSM-5 zeolite reduced in vacuum and after adsorption of

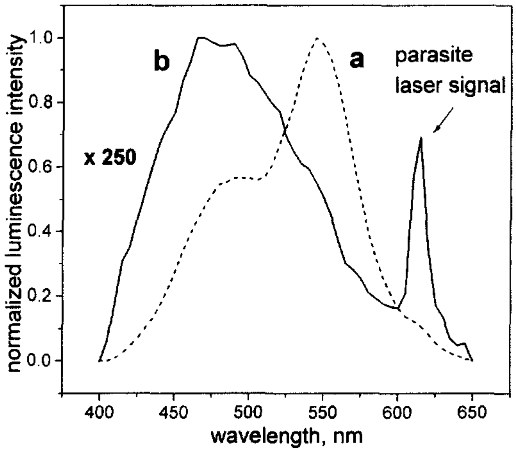

Fig. 5. Effect of NO adsorption on Cu^{+} luminescence of Cu-ZSM-5 (Si/Al 22.5, Cu/Al 0.23; reduced 2 min at 523 K in 10 Torr of H_2): (a) after evacuation at 523 K and (b) after addition of 10 Torr of NO.

NO at room temperature. The intensity of the whole spectrum was substantially quenched (decrease approx. 250×) but the Cu-IV site (Cu^+ emission at 540 nm) was much more affected compared to the site of the type Cu-II reflected in the emission at 480 nm.

4. Conclusions

The presence and number of Cu^+ ions formed in originally prepared Cu^{2+}-ZSM-5 zeolite by ion exchange depends on the zeolite treatment and Cu/Al/Si composition as documented here. It is concluded that two main different Cu sites found in high silica ZSM-5 zeolites exhibit different redox properties and reactivity with respect to NO. The Cu sites (denoted as Cu-II) possessing a higher positive charge, causing a higher electron density transfer from NO molecule to the Cu site (band at 1912 cm^{-1}), are more difficult to reduce and prefer a divalent state. The Cu sites (Cu-IV) exhibiting a lower positive charge, resulting in a lower electron density transfer from NO molecule to the Cu site (band at 1895 cm^{-1}) are more stable against oxidation and tolerate to some extent monovalent state. Simultaneously, the latter Cu sites also exhibit higher interaction with respect to adsorption of NO molecule.

Based on the assumption that the former Cu sites are charge balanced by a higher negative framework charge (two Al atoms) and the latter Cu sites are adjacent to a single Al, far remote from other framework Al atoms, to a low negative charge, a decisive role of local negative framework charge adjacent to the Cu ion, given by the distribution of Al in the zeolite framework, for the Cu ions reducibility is indicated. In addition to the effect of the local negative framework charge on the redox properties of the Cu ions there is the effect of the total negative charge given by the content of Al in the framework, Si/Al ratio. Thus the values of negative framework charges (both local and total) play an important role for the Cu ions redox properties.

Due to the redox character of the NO decomposition process a similar correlation of the Cu/Al/Si composition with the individual parameters of the Cu sites reducibility and catalytic activity in NO decomposition has been expected. It has been indicated in [4] and is given and discussed in detail elsewhere (see [9]).

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