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Differences in the structure of copper active sites for decomposition and selective reduction of nitric oxide with hydrocarbons and ammonia

B. Wichterlová^{*}, Z. Sobalík, A. Vondrová

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-182 23 Prague 8, Czech Republic

Abstract

Cu ion co-ordination-location in zeolites of MFI, erionite, mordenite matrices has been determined and the activity of the individual Cu sites compared for NO decomposition and its selective reduction by hydrocarbons or ammonia. It appears that Cu ions in the vicinity of one framework Al (site II), able to form stable Cu⁺-dinitrosyl complexes, and abundant in MFI structure, are responsible for high activity in NO decomposition. The Cu ions neighbouring two framework Al atoms (site I), and forming mostly mononitrosyl complexes, which dominate in erionite structure, provide a high activity in selective reduction of NO.

Keywords: NO reduction; Cu-zeolite catalysts

1. Introduction

Cu ions planted in zeolite matrices exhibit unique activity in NO decomposition [1,2], NO selective reduction with hydrocarbons [3] as well as with ammonia [4]. While some effort has been given so far to elucidate the mechanism of these reactions [5–7], there is a lack of information on the structure of the Cu active site. To identify various Cu sites an experimental approach combining Cu⁺ luminescence, IR spectroscopy of NO adsorbed on Cu²⁺ ions and Cu²⁺ ESR has been suggested and successfully employed [8–10]. Recently, we have identified the active Cu site for NO decomposition [2].

The aim of this study is to show differences in the character of the Cu sites active in the decomposition and selective catalytic reduction (SCR) of NO by investigating the Cu siting in Cu-ZSM-5 of various Cu/Al and Si/Al, in Cu-mordenite and Cu-erionite, and its correlation with the Cu ions redox properties and catalytic activity.

2. Experimental

Cu²⁺-zeolites were prepared by Cu ion exchange from CuCl₂ or Cu(acetate)₂ solution with Na-ZSM-5 (Si/Al 22.6 and 14.1), Na-mordenite (Si/Al 8.5) and Na-erionite (Si/Al 3.6) to obtain Cu/Al ratios from 0.16 to 0.56. The chemical composition of the prepared Cu

^{*} Corresponding author.

zeolites was determined by chemical analysis after their dissolution.

Cu^+ luminescence spectra of Cu^{2+} -zeolites reduced by hydrogen to Cu^+ -zeolites, in such a way that maximum intensity of Cu^+ was obtained, were recorded at a decay time of 5 μs , employing a kinetic spectrometer (Lambda Physik) equipped with an excimer laser (308 nm, 20 ns pulse). A detail procedure is given in Ref. [8]. IR spectra of NO adsorbed on Cu^{2+} -zeolites were monitored at 298 or 150 K on transparent plates (about 10 mg/cm²) using FT-IR Nicolet Magna-550 spectrometer.

The catalytic data were obtained on a flow-through microreactor. NO decomposition (4000 ppm + He) was carried out in a total feed of 100 ml/min and catalyst weight equal to 3.5 mg of Cu. SCR of NO by propane was measured with 1000 ppm of NO, 1000 ppm of propane, and 5.0 vol.-% of O₂ in He and catalyst weight equal to 3.5 mg of Cu. SCR of NO by ammonia (4000 ppm of NO, 4000 ppm of NH₃, 3.0 vol.-% of O₂ in He) was performed at a total feed of 500 ml/min and catalyst weight of 4.1 mg of Cu.

3. Results and discussion

Cu loaded zeolites of MFI, erionite and mordenite structures with various Cu concentrations and Si/Al ratios have been used to investigate the effect of different Cu co-ordinations on the activation of NO molecules and Cu-zeolite activity. Cu^+ luminescence, IR spectra of adsorbed NO on Cu^{2+} and Cu^{2+} ESR spectra have appeared to be highly sensitive to the co-ordination the Cu sites in the zeolite matrices. Figs. 1 and 2 illustrate the Cu^+ emission and Cu^{2+} -NO vibration bands in zeolites.

The spectra indicate two main Cu co-ordinations in the MFI matrix, differing in population in dependence on the Cu concentration (Fig. 3) and content of aluminum in the framework (Si/Al) (cf. Ref. [8]). The deconvolution was made using Gaussian distribution. The Cu^+

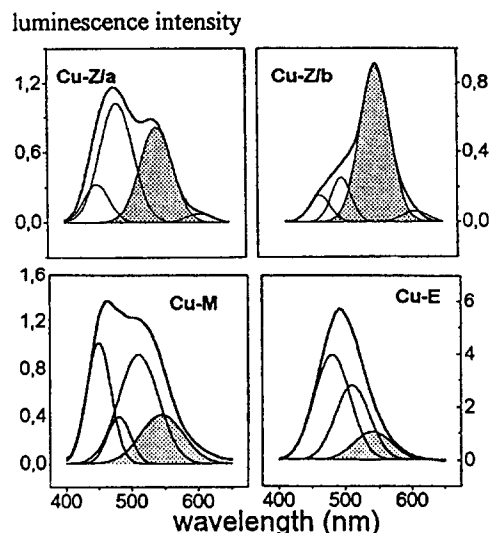


Fig. 1. Cu^+ luminescence spectra of Cu-ZSM-5 with Si/Al 14.1 and Cu/Al 0.20 (Cu-Z/a), Si/Al 22.6 and Cu/Al 0.26 (Cu-Z/b), Cu-mordenite with Si/Al 8.5 and Cu/Al 0.17 (Cu-M), and Cu-erionite with Si/Al 3.6 and Cu/Al 0.19 (Cu-E).

emission band at 540 nm and IR of NO at 1896 cm^{-1} are indicated as shadow areas and correspond to the Cu-II site important for high silica zeolites and NO decomposition (see below).

The Cu site of the type (I) (Table 1) with an IR band of Cu-NO at 1912 cm^{-1} , Cu^+ emis-

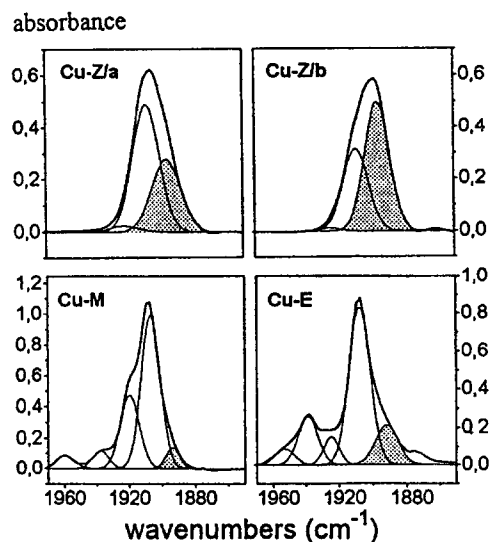


Fig. 2. IR bands of nitrosyl species of NO adsorbed on Cu^{2+} of Cu-ZSM-5 with Si/Al 14.1 and Cu/Al 0.20 (Cu-Z/a), Si/Al 22.5 and Cu/Al 0.26 (Cu-Z/b), Cu-mordenite with Si/Al 8.5 and Cu/Al 0.17 (Cu-M), and Cu-erionite with Si/Al 3.6 and Cu/Al 0.19 (Cu-E).

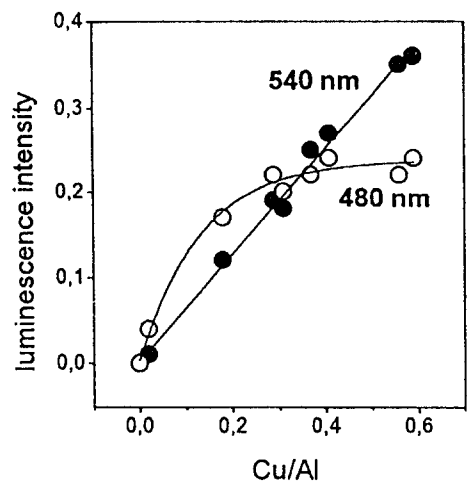


Fig. 3. Dependence of the Cu⁺ luminescence intensity of individual bands on the Cu loading of ZSM-5.

sion at 480 nm and ESR of Cu²⁺ with the parallel component $g_{\parallel} = 2.32$ and $A_{\parallel} = 150$ G, with pyramidal ligand field symmetry, was ascribed to the single Cu²⁺ ion in the vicinity of two framework Al atoms, balancing Cu divalent charge [10]. This site is preferably occupied (Fig. 3).

The Cu site of type (II) exhibiting IR band of Cu²⁺-NO at 1896 cm⁻¹, Cu⁺ emission at 540 nm and ESR signal with the parallel component

$g_{\parallel} = 2.27$, $A_{\parallel} = 170$ G was ascribed to the planar Cu ion co-ordination in vicinity of one framework Al atom. These Cu²⁺ species should contain an extra framework oxygen ligand and prevail at high Cu loading and in zeolites of high Si/Al (see Table 1). It is assumed that the Cu ions preserve their bonding adjacent to two or one framework Al atom regardless of their divalent or monovalent state. The Cu ions in erionite are nearly exclusively Cu sites of (I) type, while those in mordenite matrix contain besides the Cu-I sites, some lower proportion of the sites (II) and in addition the sites with the luminescence at 450 and 510 nm, denoted as Cu-III and Cu-IV; for detail discussion of their co-ordination and redox properties see Ref. [9] and [10].

3.1. Cu ion siting and redox properties

The most populated sites in ZSM-5 are Cu-I and Cu-II sites, which differ dramatically in redox behavior. Fig. 4 illustrates differences in behavior of Cu in erionite, where the Cu-I sites prevail and in ZSM-5, with a population of both Cu-I and Cu-II sites.

Table 1
Characterisation of Cu-I and Cu-II sites at zeolites

Cu site denoted	Cu ⁺ emission (nm)	IR Cu ²⁺ -NO (cm ⁻¹)	ESR		Al local arrangement	Cu ²⁺ co-ordination ^a
			g_{\parallel}	A_{\parallel} (G)		
Cu-I	480	1912	2.33	150–160	Al-pairs	square pyramidal
Cu-II	540	1895	2.28	180	single Al	square planar

^a Attributed according to Ref. [11].

Table 2
Cu siting vs. activity for SCR of NO by propane on zeolites

Zeolite	Si/Al	Cu/Al (wt.-%)	Cu-total (wt.-%)	Cu-II	NO conversion (%)
Erionite	3.60	0.16	2.93	0.2	16
Mordenite	8.51	0.11	1.62	~ 0.2	38
ZSM-5	22.6	0.51	2.00	1.70	73
ZSM-5	14.1	0.44	2.87	1.38	71

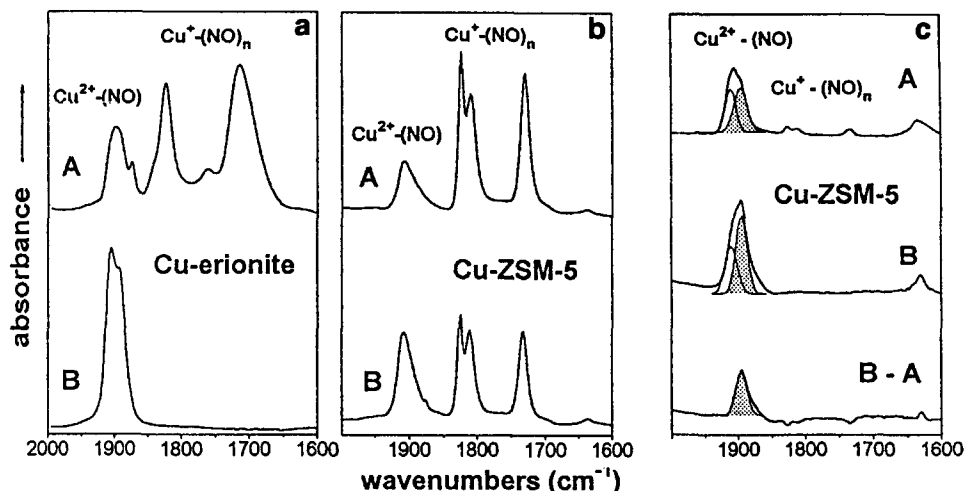


Fig. 4. (a),(b) IR bands of NO (42 Torr) adsorbed on Cu-erionite (Si/Al 3.6, Cu/Al 0.26) and Cu-ZSM-5 (Si/Al 22.6, Cu/Al 0.48) on samples reduced by CO (100 Torr, at 725 K for 2.5 h and evacuated at the same temperature for 3 h), measured at 150 K (A) and after a temperature increase to 280 K in NO atmosphere (B). (c) IR bands of NO (42 Torr) adsorbed on Cu-ZSM-5 oxidized in oxygen (42 Torr, 725 K for 3 h) (A) and after temperature increase to 550 K in NO (B) and their difference (B - A).

Substantially higher stability of the Cu^+ -dinitrosyl species on ZSM-5, when compared to erionite, was revealed by their basically different behavior during low temperature and ambient temperature experiments (see Fig. 4a,b). As indicated on Fig. 4c, the prevailing role of the Cu-II site species at the stabilization of the Cu^+ -dinitrosyl species of Cu-ZSM-5 is obvious.

Thus, the redox properties of the Cu ions are controlled by the local framework Si-Al sequences, however an overall Si/Al ratio, yielding a total negative framework charge, affects additionally the reducibility of the individual Cu ion. It follows that the Cu ions (site II), balanced by the single framework Al atom, are the most stable in monovalent state and interact strongly with NO with formation of dinitrosyl complexes.

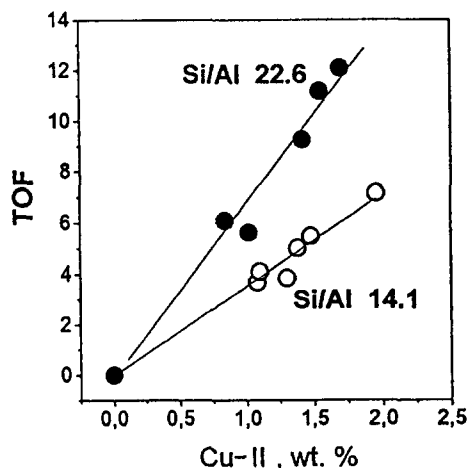


Fig. 5. The effect of concentration of Cu-II site on TOF (molecule/Cu atoms s) for NO decomposition over Cu-ZSM-5.

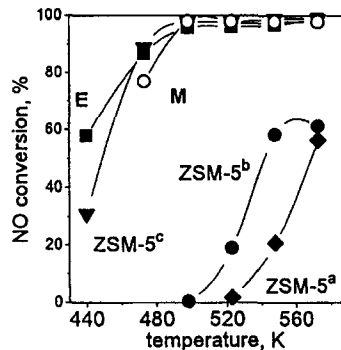


Fig. 6. NO conversion at SCR by ammonia on Cu-erionite with Si/Al 3.6, Cu/Al 0.16 (E), Cu-mordenite with Si/Al 8.5, Cu/Al 0.38 (M) and Cu-ZSM-5 with Si/Al 22.6, Cu/Al 0.33 (a), Si/Al 17.3, Cu/Al 0.20 (b), and Si/Al 14.1, Cu/Al 0.56 (c).

3.2. Catalytic properties

Fig. 5 depicts dependence of turn over frequency of NO molecule per Cu atom for Cu-ZSM-5 of various Cu/Al and Si/Al ratios on the concentration of the Cu-II sites, the Cu ions balanced by a single framework Al atom. A linear relationship clearly evidences that the active sites for NO decomposition are the Cu-II sites. A splitting of the dependence into two lines reflects the effect of the overall negative framework charge. The Cu-II sites in a zeolite of a lower negative charge (higher Si/Al) are more active as their tendency to the monovalent state is supported by a higher Si/Al ratio.

The unique role of the Cu-II site found in NO decomposition was not equally manifested in the NO selective reduction by NH₃ or propane. With SCR of NO by ammonia (see Fig. 6) the Cu sites balanced by Al pairs should also participate in the catalytic reaction to explain their high activity of Cu-erionite and Cu-mordenite containing low number of the Cu-II sites (cf. Table 2). As for the selective reduction of NO with propane, contribution of both the Cu centers of types (I) and (II) should also be anticipated, as follows from Table 2.

4. Conclusions

Cu siting in high silica zeolites is controlled by the local Si–Al sequences in the framework. The redox properties of the Cu ions depend on both the local Si–Al sequence and total framework charge. The Cu sites neighbouring one framework Al atom display unique tendency to

monovalent state, which is higher in zeolites of low negative framework charge.

The Cu sites balanced by a single framework Al are the active sites for NO decomposition, while in selective catalytic reduction of NO with ammonia or propane the role of the other Cu sites, adjacent to Al framework pairs, should be anticipated.

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