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IR studies and DFT calculations concerning the status of Cu^+ ions in CuZSM-5 and CuMCM-41

J. Datka*, P. Kozyra, E. Kukulska-Zając

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

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Abstract

The average electron donor properties of Cu^+ ions in CuZSM-5 were found to be stronger than in CuMCM-41. This was evidenced by IR studies of CO, N_2 and NO adsorption. The stronger electron donor properties of Cu^+ the stronger it activates adsorbed molecules by π-back donation. This is why Cu^+ ions in CuZSM-5 are more active in "deNOx" reaction than in CuMCM-41. IR studies of CO and N_2 desorption showed that Cu^+ ions in both CuZSM-5 and CuMCM-41 were heterogeneous and the Cu^+ sites of various electron donor properties were present. Quantumchemical DFT calculations showed that the electron donor properties of Cu^+ (electrical charge and energy of HOMO) depend on the location of Cu^+ in zeolites. Cu^+ ions in α sites (of higher number of oxygen atoms surrounding the cation) are stronger electron donor than Cu^+ ions in β sites. The calculations evidenced also that Cu^+ in α sites activate stronger NO molecules than in β sites.

Keywords: DeNOx; CuZSM-5; CuMCM-41; IR spectroscopy; DFT calculations

1. Introduction

CuZSM-5 as well as other Cu containing zeolites have been extensively studied because of their activity in "deNOx" process (e.g. review papers [1–7]). CuMCM-41 was found to be less active in "deNOx" [8], but it was found to be active towards several organic molecules. It was found active in but-1-ene isomerization and isobutene formation [9,10] as well as in other reactions interesting for fine chemistry (e.g. [11,12]). The quantumchemical calculations showed [13,14], that the "deNOx" activity could be related to electron donor properties of Cu^+ in zeolites, and π-back donation of d electrons of Cu^+ to π^* antibonding orbitals of NO, which resulted in a distinct N–O bond weakening. It has been found recently [15,16] that Cu^+ ions in zeolites were also able to activate alkene molecules by π-back donation.

The electron donor properties of Cu cations in zeolites are the most important in the activation of both NO and organic molecules. Two problems have been investigated in this study: comparison of electron donor properties of Cu^+ as well as the problem of heterogeneity of Cu^+ ions in CuZSM-5 and CuMCM-41.

The electron donor properties of Cu^+ were studied by IR spectroscopy by comparison the frequencies of stretching vibrations of CO, N_2 and NO. The information on heterogeneity of Cu^+ sites was obtained by following (by IR spectroscopy) the desorption of CO and N_2. We carried out also quantumchemical DFT calculations in order to study how the location of Cu^+ ions in zeolite influences these properties of Cu^+ ions which control the electron donor properties (electric charge, HOMO energy) as well as on NO activation.

2. Experimental

In order to obtain Cu-zeolites, parent NaZSM-5 (Si/Al = 35 synthesized at the Institute of Industrial Chemistry, Warsaw) and MCM-41 (Si/Al = 15, synthesized at Turku University) were used. NaZSM-5 zeolite was treated with $(CH_3COO)_2Cu$ solution at 350 K, CuZSM-5 was subsequently washed with hot water. Cu content was 1.4%, which corresponded to Cu/Al = 0.48. CuMCM-41 was obtained by the treatment of HMCM-41 with $Cu(NO_3)_2$ solution and subsequently washed with hot water. Cu content was 2.3%.

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* Corresponding author. Tel.: +48 12 6336377; fax: +48 12 6340515.
E-mail address: datka@chemia.uj.edu.pl (J. Datka).

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In the IR studies zeolites were activated in vacuum at 770 K for 1 h. CO and NO were adsorbed at room temperature whereas N_2 at 170 K. IR spectra were recorded with a BRUKER 48 PC spectrometer equipped with a MCT detector (resolution 2 cm^{-1}). The IR spectra have been recorded at the adsorption temperature, except of desorption experiments in which the spectra were recorded at temperature range: 170–250 K for N_2, and room temperature −600 K for CO.

2.1. Calculation method

DFT calculations were carried out for cluster models by Dmol Software of MSI© [17]. Dmol code is the implementation of a numerical scheme for solving Kohn-Sham equations. We have chosen standard calculation parameters e.g. local VWN exchange-correlation potential and numerical DNP basis set. Inner core orbitals were frozen during calculations. This choice was a compromise between computational efficiency and expected accuracy. The properties to be discussed herein are certain geometrical parameters, charge distribution, N–O stretching frequency and NO adsorption energy.

Two models of the copper site were cut out from the MFI structure: (i) basket (M7) model comprised of 7T atoms arranged into two fused 5T rings forming a 6T ring for copper α site and (ii) deformed 6T ring postulated as the environment for β copper positions. The Cu^+ cation was then placed in the centre in the 6T ring and its position of both clusters was optimized with constrained coordinates of protons terminating the cluster.

3. Results and discussion

3.1. Average electron donor properties of Cu^+ in CuZSM-5 and CuMCM-41

The average electron donor properties of Cu^+ was studied by comparing the values of stretching frequencies of adsorbed CO, N_2 and NO. CO and NO were adsorbed at room temperature and N_2 at 170 K. The adsorption of CO and N_2 was carried out by the introduction of excess of these gases into the cell (about 1 Torr in gas phase), followed by a short evacuation at the adsorption temperature. In the case of NO which oxidizes Cu^+ to Cu^{2+} small doses of NO were introduced at room temperature into the cell until the band at 1812–1815 cm^{-1} attained a maximum intensity. The determined values of stretching frequencies of CO, N_2 and NO adsorbed in CuZSM-5 and CuMCM-41 are presented in Table 1.

Table 1
The frequencies of CO, N_2 and NO adsorbed on CuZSM-5 and CuMCM-41

Zeolite	Frequencies of adsorbed molecules (cm^{-1})		
	CO	N_2	NO
CuZSM-5	2157	2295	1812
CuMCM-41	2160	2300	1815

For all three probe molecules the frequencies are smaller for Cu^+ in CuZSM-5 than in CuMCM-41. Generally, the frequencies of CO, N_2 and NO adsorbed on Cu^+ cations are lowered due to π-back donation of d electrons from Cu^+ ions to antibonding π* orbitals of the molecule. The stronger the electron donor properties of the ion, the stronger the π-back donation effect and the lower the stretching frequency of all three molecules.

However, in the case of CO, an additional effect: a σ-donation of σ electrons of CO to the adsorption site should be also considered. As the σ orbital of CO has slightly antibonding character, σ−donation strengthens the CO bond and shifts its frequency up. The less electron acceptor (i.e. more electron donor) the adsorption site is, the weaker is the σ-donation, and the lower is the stretching frequency. Therefore, all the factors that enhance the electron donor properties of Cu^+ ions in zeolites contribute to decrease the stretching frequency of C–O bond (because of increase of π-back donation and decrease of σ-donation).

The results presented in Table 1 showing the lower stretching frequencies of CO, N_2 and NO adsorbed on Cu ZSM-5 indicate, that average electron donor properties of Cu^+ in CuZSM-5 are stronger compared to CuMCM-41. Generally, the electron donor properties of Cu^+ cation in zeolites as well as of other cations (e.g. of Co^{2+} [17]) are strongly modified by electron transfer from the framework (which plays the role of electron reservoir [7]) to the cation. It results in a distinct lowering of the effective charge of cation: from +1 to about +0.3 (vide infra) for Cu^+ or from +2 to 0.68–0.8 for Co^{2+} [17]. It can be postulated that the stronger average electron donor properties of Cu^+ in CuZSM-5 compared to CuMCM-41 may be the result of a more effective neutralization of the cation charge by the framework oxygen atoms in the case of ZSM-5.

The stronger electron donor properties of Cu^+ in CuZSM-5 than in CuMCM-41 indicate, that the ability to activate molecules by π-back donation of d electrons to π* antibonding molecular orbitals is also higher in the case of CuZSM-5. Such activation of the molecule weakens its double or triple bond and makes the molecule more prone to the dissociation and to other reactions. It also explains the higher activity of CuZSM-5 compared to CuMCM-41 in the decomposition of NO [8], in which NO is activated by π-back donation.

3.2. Heterogeneity of Cu^+ sites in CuZSM-5 and CuMCM-41

The problem of heterogeneity of Cu^+ sites in both CuZSM-5 and CuMCM-41 was studied by following the desorption of CO and N_2 by IR spectroscopy. The excess of CO and N_2 was adsorbed at room temperature and at 170 K, respectively. The spectra were then recorded upon the evacuation at the temperatures in the range: from room temperature to 600 K for CO and 170–250 K for N_2. The spectra corresponding to CO desorption from both CuZSM-5 and CuMCM-41 and to N_2 desorption from CuZSM-5 are presented in Fig. 1. The initial intensities of Cu^+–N_2 bands in the case of CuMCM-41 was so low, that upon the partial desorption from CuMCM-41 they were poorly discrenible in the spectra.

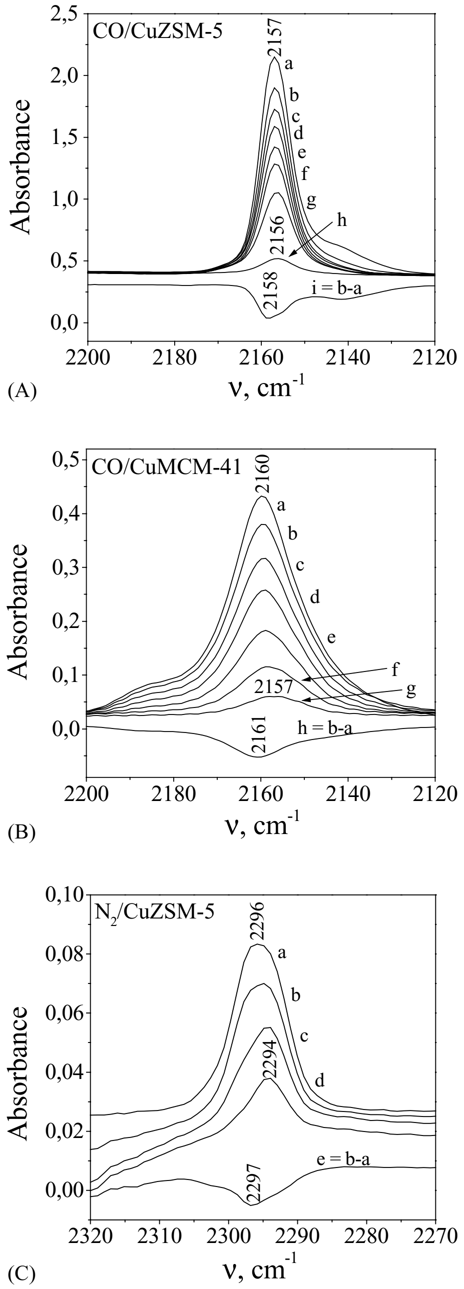

Fig. 1. (A) IR spectra of CO adsorbed on CuZSM-5 at room temperature and desorbed at: (a) 300 K, (b) 320 K, (c) 370 K, (d) 390 K, (e) 410 K, (f) 425 K, (g) 510 K, (h) 600 K, difference spectrum b − a. (B) IR spectra of CO adsorbed on CuMCM-41 at room temperature and desorbed at (a) 300 K, (b) 320 K, (c) 340 K, (d) 360 K, (e) 380 K, (f) 410 K, (g) 430 K, (h) difference spectrum b − a. (C) IR spectra of N_2 adsorbed on ZSM-5 at 170 K (a) and desorbed at (b) 200 K, (c) 230 K, (d) 250 K, (e) difference spectrum b − a.

The spectra presented in Fig. 1 show a small shift to lower frequencies of the bands of CO and N_2 still present in zeolites with the desorption temperature. The band shift is better seen when comparing the spectra recorded for the desorption at the highest temperatures (spectra h, g and d in Figs. 1A–C, respectively) representing the most strongly bonded molecules with the differential spectra: i, h and e representing the molecules the most weakly bonded to Cu^+, i.e. desorbing at the lowest temperatures. The band shift seen in Fig. 1 indicates, that in both CuZSM-5 and CuMCM−41 there are Cu^+ cations of stronger electron donor properties, and therefore of stronger π-back donation effect, which bond CO and N_2 more strongly and decrease more the stretching frequency of C–O and N–N vibration. There are also the cations of weaker electron donor properties, and therefore of weaker π-back donation effect.

It may be postulated, that the sites of various electron donor properties in CuZSM-5 and in CuMCM-41 will show different activity in "deNOx" due to different π-back donation abilities.

According to the data presented in Fig. 1A and B, the frequency difference between the stretching frequencies of CO desorbing at the lowest and highest temperatures is higher in the case of CuMCM-41 (4 cm^{-1}) than for CuZSM-5 (2 cm^{-1}), suggesting, that the distribution of Cu^+ sites of various electron donor properties is broader in CuMCM-41. This statement is further supported by larger width of the band corresponding to CO adsorbed on CuMCM-41 (Fig. 1A and B). The broader distribution of sites of various electron donor properties in CuMCM-41 may be explained by a greater variety (heterogeneity) of possible environments of Cu^+ ions in amorphous MCM-41 structure than in crystalline ZSM-5 zeolite.

It is possible that the difference in electron donor properties of Cu^+ in both CuZSM-5 and CuMCM-41 may be explained by the presence of Cu^+ in the sites in which they have different number of oxygen atoms in close proximity and by the fact that the electrical charge of Cu^+ cations may neutralized to a various degree by framework oxygens. This will be examined in details by DFT quantumchemical calculations.

3.3. The properties of Cu^+ in various sites in CuZSM-5 zeolite

The properties of Cu^+ cations in sites with different number of surrounding oxygens, and their interaction with NO molecules were the subject of DFT calculations. Two clusters were constructed (Fig. 2A and B): one consisting of two five-member rings, forming one six-member ring (denoted as site α), and another one being a deformed six-member ring (site β). According to Wichterlova et al. [18,19] the sites α and β are the most probable locations for Cu^+ ions

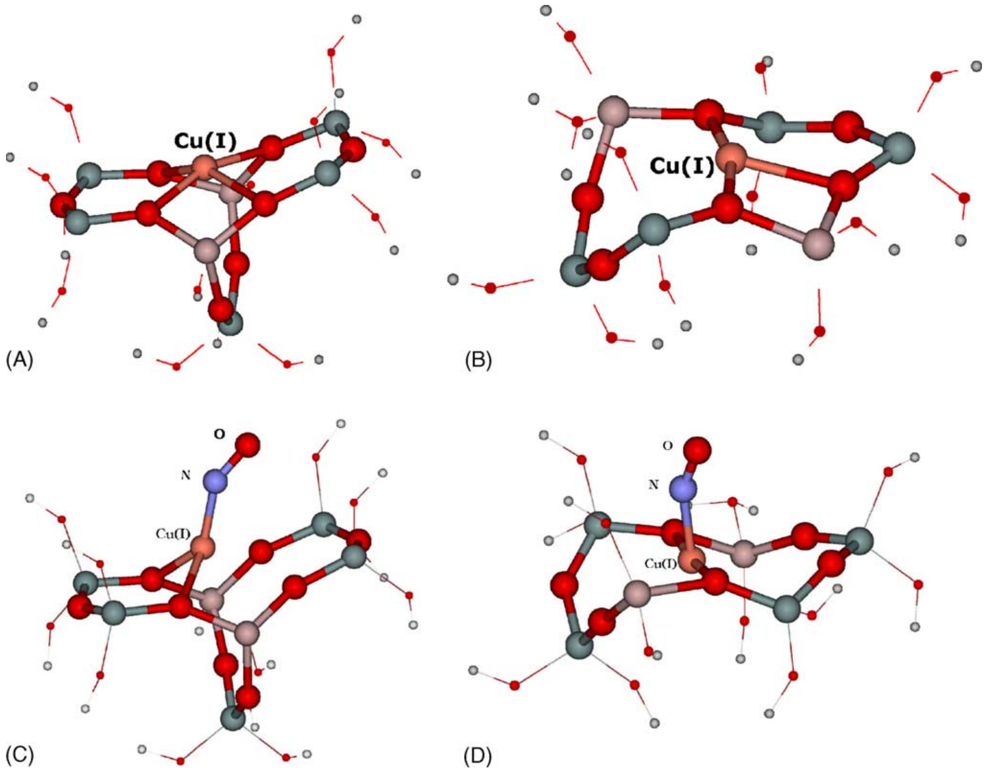

Fig. 2. (A, B) Cluster models of copper(I) cationic sites denoted as: α and β. (C, D) The same clusters with NO adsorbed.

in the ZSM-5 zeolite. Both α and β clusters contained two Al atoms and one Si–OH–Al bridging hydroxyl balancing (in addition to Cu^+ cation) negative charge of AlO_4^- tetrahedra.

The obtained values characterizing the electron donor properties of Cu^+ in α and β clusters: the electrical charge and the energy of HOMO, are presented in Table 2. The positive charge is lower and HOMO energy is higher if Cu^+ is located in the α site, indicating that Cu^+ in α sites are stronger electron donor than those in β sites. Most probably this is a consequence of more dense oxygen packing around Cu^+ in α sites. The results of DFT calculations explain therefore observed heterogeneity of Cu^+ sites and the presence of Cu^+ sites of various electron donor properties (Fig. 1).

The next step of our calculations was the examination of the interaction of Cu^+ in the α and β sites with NO molecules. In these calculations (in contrast with our earlier approach [14]) the hydroxyl group neutralizing AlO_4^- was so far from NO molecule (Fig. 2A), that no hydrogen bonding O–H···NO was not formed. The optimized clusters of Cu^+ in α and β sites with NO are presented in Fig. 2C and D. The interaction of Cu^+ with NO results in breaking of some bonds between Cu^+ and framework oxygen. The calculated parameters characterizing the interaction of Cu^+ with NO are also presented in Table 2. The positive charge of Cu^+ increases (by 0.05–0.08 e) upon NO adsorption indicating a π-back donation of electrons from Cu^+ to the NO antibonding orbitals. This effect is stronger in the case of Cu^+ in α sites with stronger electron donor properties (of higher HOMO energy). As a consequence, the activation of NO takes place resulting in some N–O bond lengthening and in the decrease of N–O stretching frequency. This effect is stronger in the case of α sites. The NO adsorption energy is also higher for α sites.

All of the DFT calculation results indicate, that Cu^+ cations located in α sites, in which they have more oxygens in close proximity are stronger electron donor than

Table 2
Calculated properties of Cu^+ in sites α and β in CuZSM-5 zeolite: electrical charge (q_{Cu}), energy of HOMO (E_{HOMO}) and of the complexes of NO bonded to Cu^+: change of electrical charge on Cu^+ (Δq_{Cu}), N–O bond distance ($R_{N–O}$), NO stretching frequency ($\nu_{N–O}$), and NO adsorption energy (E_{adsNO})

	Without NO		With NO			
	q_{Cu}	E_{HOMO} (eV)	Δq_{Cu}	$R_{N–O}$ (nm)	$\nu_{N–O}$ (cm^{-1})	E_{adsNO} (kJ/mol)
Cu^+, α site	0.28	−5.170	+0.08	0.119	1754	100
Cu^+, β site	0.32	−5.317	+0.05	0.118	1778	71

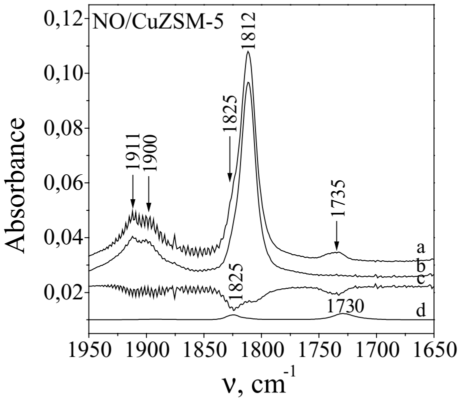

Fig. 3. (a) IR spectra of NO adsorbed at room temperature on CuZSM-5, (b) upon the evacuation at room temperature, (c) differential spectrum b − a, (d) the spectrum of dinitrosyls $Cu^+(NO)_2$ normalized to the same intensity of 1735 cm^{-1} band as in the spectra (a) and (b).

in β sites. Cu^+ in α sites bond stronger and activate more NO molecules by π-back donation. It may be also expected that besides NO, Cu^+ in α sites would also activate other molecules, according to the same mechanism.

According to the results presented in Table 2 the stretching frequencies of NO bonded to α and β sites (1754 and 1778 cm^{-1}) differ by 24 cm^{-1}. Such a difference should be seen in IR spectrum as a splitting of the band of NO adsorbed in CuZSM-5.

The spectrum of NO adsorbed on CuZSM-5 (Fig. 3 spectrum a) shows a band of Cu^+NO mononitrosyls at 1812 cm^{-1} with a shoulder at 1825 cm^{-1} and another weak band at 1735 cm^{-1}. The latter is the band of symmetric vibration of $Cu^+(NO)_2$ dinitrosyls. The shoulder at 1825 cm^{-1} is a band of antisymmetric vibrations of dinitrosyls, but it may be also a second band of Cu^+NO mononitrosyls. Short evacuation at room temperature removes both the 1735 cm^{-1} band and 1825 cm^{-1} shoulder (Fig. 3, spectrum b). This is well seen in the difference spectrum (c) (obtained by subtraction of the spectrum upon evacuation from the spectrum before evacuation). The spectrum of $Cu^+(NO)_2$ dinitrosyls (formed by the adsorption of NO on CuZSM-5 at 170 K) normalized to the same intensity of 1735 cm^{-1} is also presented (spectrum d). The "intensity" of the 1825 cm^{-1} minimum in difference spectrum (c) is about three times higher as in the spectrum of dinitrosyls (spectrum d). It suggests that the shoulder at 1825 cm^{-1} in the spectrum of NO adsorbed on CuZSM-5 may be a superposition of the band of dinitrosyls and the band of the second type of mononitrosyls. The results presented in Fig. 3 suggest therefore, that two kinds of Cu^+NO mononitrosyls (characterized by the bands at 1812 and 1825 cm^{-1}) may be present in the case of CuZSM-5. It is not be ruled out, that they may correspond to Cu^+ in α and β sites. In this latter case the band at the lower frequency 1812 cm^{-1} may be related to Cu^+ in the α sites in which the π-back donation effect is more important, and NO is more strongly bonded to Cu^+ (as evidenced by DFT calculations), and the band at 1825 cm^{-1}—to Cu^+ in the β sites (less activating and weakly bonding NO). The frequency difference between these two bands is 13 cm^{-1}. The agreement between the experimental vales (13 cm^{-1}) and the value obtained from quantumchemical DFT calculations (24 cm^{-1}) is rather satisfactory, taking into account the accuracy of DFT calculations.

It should be noted, that according to the best of our knowledge, the presence of more than one kind of Cu^+NO mononitrosyls in CuZSM-5 was not reported before.

4. Conclusions

IR studies of CO, N_2 and NO adsorption showed stronger average electron donor properties of Cu^+ in CuZSM-5 than in CuMCM-41. This implies stronger activation of adsorbed molecules by π-back donation and therefore explains higher catalytic activity of CuZSM-5 in the decomposition of NO than of CuMCM-41.

IR experiments of CO and NO desorption evidenced heterogeneity of Cu^+ in both CuZSM-5 and CuMCM-41, i.e. the presence of Cu^+ of various electron donor properties. Quantumchemical DFT calculations performed with CuZSM-5 explained this by the presence of Cu^+ in sites of different number of oxygens surrounding the cation (sites α and β). DFT calculations showed that Cu^+ in sites α have lower positive charge and higher energy of HOMO, thus they show higher ability of π-back donation and activation of adsorbed molecules. In CuMCM-41, the DFT calculations could not be carried out, because the environment of Cu^+ ions in not known, but we suppose, that the reason of heterogeneity of Cu^+ sites is in similar as in CuZSM-5.

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