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Why Cu^+ in ZSM-5 framework is active in $DeNO_x$ reaction—quantum chemical calculations and IR studies

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Abstract

In this paper, we present quantum chemical calculations for copper sites in the extended model of ZSM-5 framework based on seven T sites in two fused 5T rings cut off the MFI structure. Geometrical and electronic properties of cationic copper centres and their adsorption complexes with NO molecule are analysed from the point of view of the activation mechanism. The calculations show that the NO molecule adsorbed on Cu^+ site becomes significantly activated contrary to Cu^{2+} centre, in full accordance to IR measurements. Our results indicate clearly that the ability of Cu^+ site to donate electrons to π-antibonding orbital of NO causes significant bond weakening and makes Cu^+ZSM-5 active in decomposition of nitrogen oxides. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Quantum chemical calculations; Activation mechanism; Cu^+ZSM-5; Nitrogen oxides

1. Introduction

Cu^+ site in Cu^+ZSM-5 is well known to be active in decomposition of nitrogen oxides. Many research groups have studied its catalytic activity but the mechanism has not yet been understood. The location, properties of cationic sites and their interaction with guest molecules are of special interest. Although the properties of exchanged copper cations in zeolite framework have been studied by using various methods such as EPR spectroscopy [1–3], or IR spectroscopy by using probe molecules CO or N_2 [4–7], little is still known about their structure. XRD which is useful for Al-rich zeolites has several limitations in the case of high siliceous zeolites because of low cation content and low symmetry of zeolite framework [8,9]. On the other hand, the knowledge on the structure of the active centre is of prime importance for elucidation of CuZSM-5 catalytic activity.

Thus a question has still been open as to which factors were responsible for exceptional properties of Cu^+ cations in ZSM-5 framework making them different from copper cations deposited on various surfaces or in oxides. To shed some light on this problem, we have undertaken combined studies involving both experiment and quantum chemical modelling to determine copper coordination in the framework and its influence on the adsorption and activation ability of the site.

IR experiment quoted here concerned stretching frequencies of the NO molecule adsorbed on Cu^+- and Cu^{2+}-exchanged cations [10]. Quantum chemical modelling became recently well-recognised complementary tool to study properties of zeolites [11–17]. Our quantum chemical calculations were aimed at electronic and geometrical properties of both copper centres in the cluster model of ZSM-5 framework.

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In this paper, we are going to show explicit differences between coordination of Cu^+ and Cu^{2+} cations which emerge from model cluster calculations. On the other hand, the analysis of the electronic structure of the two sites should explain differences in their ability to withdraw or donate electrons to prospective adsorbates. In particular, we will show that almost perfect match between the positions of the Fermi level of Cu^+ZSM-5 and NO molecule, together with proper symmetry of the interacting orbitals, should be responsible for strong π-backdonation in this case, which seems to be crucial in the process of NO activation.

2. Experimental

CuZSM-5 zeolite was obtained by the classical ion exchange of a parent sample $Na_{2.0}H_{0.5}[(AlO_2)_{2.5}(SiO_2)_{93.5}]$ in a copper acetate solution at room temperature. The exchange degree (Cu/2Al) determined by AAS was 106%. It is well known that Cu^{2+} ions in CuZSM-5 are reduced to Cu^+ during the pre-treatment procedure. The fact that in our zeolite the exchange degree Cu/2Al = 1.06 exceeds 100% indicates that more than half AlO_4 tetrahedra (53%) are neutralised by Cu^+ and remaining tetrahedra are neutralised by protons (the Si–OH–Al band is also present in IR spectrum).

For IR studies, the zeolite was pressed into thin wafers and pre-treated in situ in IR cell at vacuum at 770 K for 1 h. NO (Linde) was used without further purification. In IR experiments, the gases were sorbed at room temperature or at 170 K. IR spectra were recorded with a Bruker 48 IFS spectrometer equipped with an MCT detector.

3. Quantum chemical modelling

DFT calculations were carried out by means of Dmol software of Molecular Simulations© [18]. The cluster model of ZSM-5 was based on seven T sites in two fused 5T rings forming a basket (Fig. 1a) cut off the MFI structure taken from databases included in the software. Two silicones at 5T rings' junction were substituted by aluminium, with two protons put on the nearest bridging oxygen to keep system neutrality. Terminal OH^- groups saturated each T site. Next Cu^{2+} and Cu^+ cations were substituted for two or one protons. Geometry of each system was optimised with constrained positions of terminal hydrogen in saturating OH groups to mimic the influence of the surrounding framework on the cluster geometry. In the final step, NO molecule was positioned in the bonding distance from both Cu sites and the geometry was re-optimised. Electronic properties were extracted from the charge redistribution, analysis of the character of frontier orbitals and from electron distribution provided by density-of-states diagrams. Stretching frequencies of NO molecule were calculated by performing full vibrational analysis for optimised adsorbed systems.

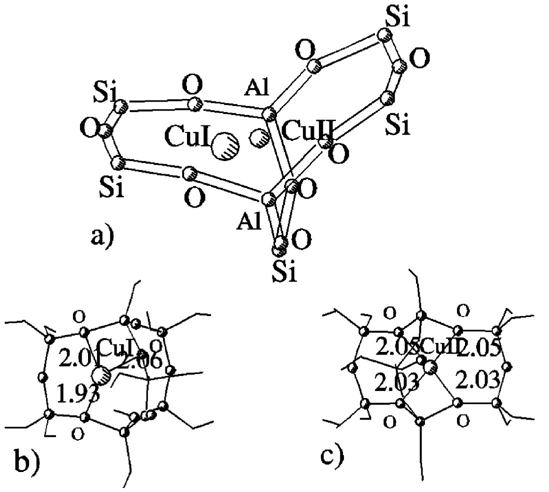

Fig. 1. (a) Schematic view of a basket model with marked positions of Cu^+ and Cu^{2+}, (b) Cu^+ site as seen from bottom of the model cluster (5T-ring side), and (c) Cu^{2+} site as seen from top of the model cluster (6T-ring side); distances between copper cation and bridging oxygen shorter than 2.5 Å are given to indicate copper coordination.

Validity of our approach (quantum chemical DFT methodology and 5T- or 6T-ring cluster models of ZSM-5 framework) has already been confirmed by us in our previous papers [10,19].

4. Results and discussion

Fig. 1 shows the optimised structures of cluster models describing Cu^{2+} and Cu^+ sites: final positions of both cations in a basal cluster (a), Cu^+ site as seen

Table 1
Properties of copper sites in ZSM-5

	$R_{\text{cu–O}}$ (Å)[a]	Q_{cu}[b]	$\varepsilon_{\text{HOMO}}$ (eV)[c]
Cu^{2+}ZSM-5	2.03, 2.03, 2.05, 2.05	+0.50	−6.443
Cu^{+}ZSM-5	1.93, 2.01, 2.03	+0.28	−5.170

[a] Distances between copper and framework oxygen below 2.2 Å.

[b] Charge on copper.

[c] Energy of the highest occupied molecular orbital.

from 5T-ring side (b) and Cu^{2+} as seen from 6T-ring side (c). It appeared that the oxidised or reduced copper cation changes its position and coordination number. Cu^{2+} prefers fourfold square planar coordination in the centre of the 6T part of the model while Cu^{+} becomes triply coordinated in the centre of 5T ring. The process of copper migration in the zeolite framework during the reduction has already been predicted by many researches and postulated by us indirectly [10,19]. Calculations performed for the extended cluster model presented in this work give the direct indication of the copper migration in ZSM-5 structure.

Table 1 gives the comparison of important geometrical and electronic features of both copper sites in our model of ZSM-5 framework. In the second column, the distances between the cation and bridging Al–O–Si oxygen shorter than 2.2 Å are listed. The numbers confirm square coordination of Cu^{2+} and threefold coordination of Cu^{+}. The calculated partial charge on the cation given in column 3 shows that the degree of covalent bonding with the framework is large and comparable in both cases. Nevertheless, these charges close to +0.5 and +0.3, respectively, correspond indeed to reduced status of Cu^{+} site. Orbital energy of the highest, partially occupied level of Cu^{2+} site lies by 0.5 eV lower than that of the highest, fully occupied level for Cu^{+}.

Moreover, we calculated the value of the Fermi level, what provides additional information on the electronic properties of the site. Fermi level falls below the top of the valence band for Cu^{2+} and lies in the middle of forbidden band for Cu^{+}, which means that the valence band in the latter case is full. For bare cations, the Fermi level falls always within the valence band. This suggests that electron acceptor character should be prevailing in the first case while the second site should act as the electron donor. Actual acceptor–donor properties of the site must obviously depend also on the adsorbed molecule and will be discussed in detail in the next paragraphs in connection with the NO molecule. Properties of Cu^{2+} and Cu^{+} sites in CuZSM-5 discussed above at the atomic scale indicate clearly that not only geometry and coordination of the site changes in the process of reduction but also the character of the site and its prospective influence on the sorbed molecule becomes essentially modified.

In order to study actual character of the interaction of both copper sites with nitrogen oxide and its consequences on the molecule, we have calculated geometrical and electronic structure of the complexes [Cu^{2+}ZSM-5]NO and [Cu^{+}ZSM-5]NO. Table 2 lists important calculated properties of both complexes. It is clearly visible that divalent copper cation changes its coordination from square planar with four equivalent bonds to bridging oxygen, to triple coordination, similar to the reduced form of copper. Actually, the interaction with NO makes both cations similar: Cu^{2+} is reduced and Cu^{+} is oxidised by nitrogen

Table 2
Effect of NO interaction with CuZSM-5

	$R_{\text{Cu–O}}$ (Å)[a]	$R_{\text{Cu–NO}}$ (Å)[b]	E_{ads} (kcal/mol)[c]	Q_{Cu}[d]	R_{NO} (Å)[e]	Q_{NO}[f]	$\varepsilon_{\text{HOMO}}$ (eV)[g]
Cu^{2+}ZSM-5	2.02, 2.03, 2.10	1.80	40	+0.43	1.15	+0.28	−6.636
Cu^{+}ZSM-5	2.02, 2.06, 2.06	1.84	24	+0.36	1.19	−0.03	−4.704

[a] Distances between copper and framework oxygen below 2.2 Å.

[b] Distance between Cu and NO.

[c] Adsorption energy.

[d] Copper charge.

[e] Bond distance.

[f] Charge on adsorbed NO.

[g] HOMO energy of the complex.

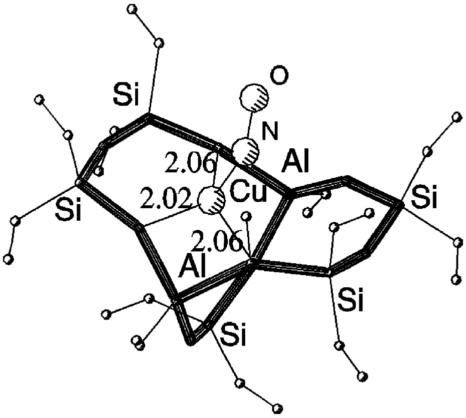

Fig. 2. Structure of Cu^+ site with adsorbed NO molecule; distances given in Å.

oxide, which was already suggested also by experiment [10,19]. The adsorption free energy calculated as the difference between total energies of both complexes and separate subsystems, is almost two times larger for Cu^{2+}ZSM-5, which is confirmed also by the bonding distance Cu–NO. Nevertheless, strong adsorption does not correspond to large activation of the molecule. On the contrary, intramolecular NO bond is shortened by 0.01 Å by the interaction with Cu^{2+} site while it is elongated by 0.03 Å on Cu^+ site. The NO bond shortening (in the case of Cu^{2+}) and bond elongation (in the case of Cu^+) correspond to bond strengthening and weakening, respectively. The NO bond elongation corresponds therefore to a distinct activation of NO molecule while interacting with Cu^+ZSM-5. Fig. 2 shows the structure of [Cu^+ZSM-5]NO complex, which is representative for both complexes (vide infra).

From electronic point of view, the process of adsorption is accompanied by the charge transfer from the NO molecule to the Cu^{2+} site and from the Cu^+ site to the NO molecule, in accordance with predicted acceptor–donor properties of both sites. In addition, the position of the highest occupied molecular orbital for [Cu^+ZSM-5]NO complex is almost equal to that of the free NO molecule (−4.762 eV), which suggests that this orbital becomes more populated. In a qualitative language, the process of NO activation on Cu^+ZSM-5 may be explained as the electron transfer to the antibonding π-orbital of NO which apparently makes the bond weaker. In the case of Cu^{2+}ZSM-5, electron transfer from the antibonding π-orbital of NO to the cation takes place, which makes the bond stronger. The relevance of electronic structure features, responsible for transferring electrons between the site and a substrate, has already been pointed out by us in the context of CO, N_2 and NO molecules interacting with copper sites in ZSM-5 [10,20]. It was shown that only the NO molecule has strongly antibonding semi-occupied orbital, which may thus accept electrons from the appropriate donor. Cu^+ in CuZSM-5 appeared to be the perfectly suited donor site for this purpose. Other molecules (CO and N_2) have no low-lying states of antibonding character to be easily populated by electrons and thus are not strongly activated over Cu^+ZSM-5 as evidenced by our DFT calculations and IR measurements [10].

Experimental measure of the activation ability of the cationic site towards adsorbed NO molecule is the shift of stretching frequency of the molecule after sorption on Cu^{2+} and Cu^+ sites in CuZSM-5 [10]. In order to relate results of theoretical modelling to IR experiment, we have calculated NO stretching frequencies for both model systems. Measured stretching frequencies of the NO molecule after sorption on Cu^{2+} and Cu^+ sites in CuZSM-5 are listed in the second column, rows 4 and 5 of Table 3. They are compared with the results of DFT calculations for cluster models described above (see columns 2 and 3). It should be stressed here that the correspondence between measured and calculated NO stretching frequencies is good indeed. This further rises credibility of our model calculations and confirms the interpretation suggested in the previous paragraphs.

Apart from measured and calculated stretching frequencies of NO adsorbed on copper sites in ZSM-5, Table 3 gives also data concerning a free molecule and calculated properties of NO interacting with free copper cations. Last column of the table lists orbital energies of the highest occupied molecular orbital in each separate system. Close inspection of the table allows for more general conclusions regarding the source of the ability of the site to activate the NO molecule. Degree of the NO bond activation seen from both shifts in its IR frequency and the change of the bond distance correlates well with the charge transfer between the site and the molecule. Important conclusion comes from the comparison of HOMO

Table 3
Measured and calculated NO stretching frequencies (ν_{NO}), changes in NO bond lengths (ΔR_{NO}) and charge on adsorbed NO (ΔQ_{NO}), values of HOMO energies for NO molecule and separate sites[a]

	ν_{NO} (cm^{-1})		ΔR_{NO} (Å)	ΔQ_{NO}	ε_{HOMO} (eV)
	Experimental	DFT			
Free NO	1876	1914	–	–	−4.762
On Cu^{2+}	–	2243	−0.05	+0.86	−30.437
On Cu^{+}	–	1890	−0.02	+0.29	−14.115
On Cu^{2+}ZSM-5	*1905*	*1904*	−0.01	+0.28	−6.443
On Cu^{+}ZSM-5	*1809*	*1754*	+0.03	−0.03	−5.170

[a] Free copper cations and cations embedded in MFI framework; values of ν_{NO} for zeolitic sites are stressed in italics.

orbital energies of copper in various valence states (Cu^{2+} and Cu^{+}) free and situated in MFI framework. Generally, HOMO orbital energy is distinctly higher for Cu^{+} than for Cu^{2+}. Further significant shift upwards occurs when situating cations in oxygen environment in MFI framework. Finally, the highest HOMO energy is observed in the case of Cu^{+}ZSM-5. In addition, this energy (−5.170 eV) is very close to the energy of the highest, partially occupied orbital of NO molecule (−4.762 eV). This close correspondence of both orbital energies makes the electron transfer from the fully occupied d-shell of Cu^{+} to the semi-occupied π-antibonding orbital of NO possible. Such an electron transfer results in a distinct weakening of NO bond seen from red-shift in stretching frequency both measured by IR spectroscopy and calculated by quantum chemistry. It results also in the activation of NO molecule in $DeNO_x$ process.

Acknowledgements

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