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The activation of C=O bond in acetone by Cu^+ cations in zeolites: IR studies and quantum chemical DFT calculations

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Abstract

Our previous IR studies as well as quantum chemical DFT calculations evidenced that Cu^+ ions in zeolites were able to activate C=C double bond in alkenes by π back donation of d electrons of Cu^+ to π^* antibonding orbitals of alkenes. It resulted in a distinct weakening of C=C bond. The present study was undertaken in order to answer the question if Cu^+ ions in zeolites were also able to activate another than C=C double bond. We studied therefore the interaction of acetone with Cu^+ in zeolites CuZSM-5, CuMCM-41, CuX and CuY. IR studies showed a weakening of C=O bond and a red shift of IR band by 39–51 cm^{-1}. The experiments in which the small doses of acetone were adsorbed as well as desorption studies evidenced that Cu^+ bonded acetone more strongly than other adsorption sites, such as hydroxyl groups. DFT modeling of the adsorption of the acetone molecule on copper site gave the information about the function of the zeolite as a host for transition metal cationic sites and as an electron reservoir. Calculated values of electron affinity and HOMO energy allowed to explain that, on the basis of the charge distribution analysis, electrons flowed from the acetone molecule to the copper site, so that the molecule was positive. It was evidenced by the analysis of the charge distribution. Therefore, the activation upon adsorption has been justified by the electronic structure of the molecule, its electron affinity as well as the ability of the site to π back donation. Moreover, the calculated value of the red shift of the IR band of the activated C=O bond was similar as experimental one.

Keywords: IR spectroscopy; Acetone; DFT calculations; Zeolites; Cu^+ cations

1. Introduction

Cu-containing zeolites attracted a great deal of attention because of their activity in the decomposition of NO [1–4]. Quantum chemical DFT calculation [5–9] evidenced that this ''denox'' activity of Cu^+ ions in zeolites could be related to the fact that the electrical charge of Cu is partially neutralized by the framework oxygen atoms. The electrical charge of Cu^+ decreased from +1 to +0.3 and HOMO energy increased from −14.115 to −4.575 eV, if Cu^+ was situated inside a cluster simulating a fragment of MFI structure.

Recently, it was found [10–12] that Cu^+ ions in zeolites CuX, CuY, CuZSM-5 and CuMCM-41 were also able to activate C=C bond in alkenes. This was evidenced by a red shift of IR band of C=C stretching by about 100 cm^{-1} and in a smaller shift of C–H bands in $=CH_2$ and =C–H groups neighboring to the double bond. Quantum chemical DFT calculations showed that this was (similarly as in the case of NO) a result of π back donation of d electrons of Cu^+ to π^* antibonding orbitals of alkenes. According to the calculation results, a part of this charge came from the Cu^+ cation itself and a part was taken from the zeolite framework which acted as a reservoir of electrons as suggested by Goursot et al. [9].

This study was undertaken to follow the interaction of Cu^+ cations in zeolites with C=O carbonyl group of acetone, being, beside alkenes, a system having empty π^* antibonding orbitals. The interaction of organic molecules containing carbonyl groups (acetaldehyde and acetone) with Si–OH–Al groups in zeolite HZSM-5 was studied by various techniques: NMR [13], IR [14], ^{13}C MAS NMR [15–19]. Experimental data evidenced stechiometric 1:1 complexes in which adsorbed molecules were bonded to hydroxyl groups by hydrogen bonding. Quantum chemical calculations [20] gave the adsorption energy of acetone adsorption (139 kJ/mol) very close to the experimental value

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(130 kJ/mol, ref. [18]). Up to now, there is no reports on the interaction of acetone with Cu^+ ions in zeolites. In this research, we studied this problem by IR spectroscopy and DFT calculations.

2. Experimental

Zeolites CuX, CuY and CuZSM-5 were prepared from zeolite NaX, NaY and NaZSM-5 synthesized in Institute of Industrial Chemistry (Warsaw) (Si/Al = 1.31, 2.56 and 35, respectively) by the treatment with $Cu(CH_3COO)_2$ solution at 350 K. Following ion-exchange the samples were washed with distilled water and dried in air at 370 K. The exchange degrees (Cu/Al) were 0.43, 0.31 and 0.45 for CuX, CuY, and CuZSM-5, respectively. We also used CuMCM-41 obtained from MCM-41 (Si/Al = 15, synthesized at Turku University) by the treatment with $Cu(CH_3COO)_2$. Cu content was 2.3 wt.%.

For IR studies, zeolites were activated at vacuum at 770 K for 1 h. Acetone (Aldrich) was adsorbed at room temperature. IR spectra were recorded with a BRUKER IFS 48 spectrometer equipped with a MCT detector (resolution 2 cm^{-1}).

2.1. Calculation method

DFT calculations were carried out for clusters models by Dmol Software of MSI© [21]. Dmol code is the implementation of 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 promoted by the compromise between computational efficiency and expected accuracy. The properties to be discussed here are geometrical parameters, charge distribution, Mayer bond orders.

A model of copper site was cut off the MFI structure. It was a basket (M7) model containing 7T atoms arranged into two fused 5T rings forming a 6T ring. The Cu^+ cation was then placed in the centre of 6T ring and its position the cluster was optimized with constrained coordinates of protons terminating the cluster.

3. Results and discussion

3.1. Electron acceptor properties of acetone

As mentioned Section 1, the embedding of Cu^+ into the cluster simulating the zeolite structure results in an increase of electron donor properties of cation. However, the phenomenon of flowing electrons from a site to an interacting molecule may be moderated by low electron affinity of the molecule. The electron affinity reveals the ability of a molecule to be an acceptor of π back donation. Thus, we have calculated by DFT method (as described above) the value of electron affinity of acetone as the difference between the total energies of an anion and of a neutral molecule. The calculated value was 0.8 eV. This value is higher than for NO (0.5 eV) but lower than for alkenes (1.4–1.5 eV), indicating that acetone is relatively good acceptor of electrons: better than alkenes, although not as good as NO.

3.2. Acetone sorption in CuZSM-5 and CuMCM-41

The results concerning the interaction of acetone with Cu^+ in CuZSM-5 are presented in Fig. 1. The spectra of acetone dissolved in CCl_4, adsorbed SiO_2 as well as sorbed in silicalite and zeolite HZSM-5 are presented as well.

Free acetone molecule (acetone dissolved in CCl_4—Fig. 1, spectrum a) shows a distinct band at 1718 cm^{-1}. The sorption of acetone in silicalite (spectrum b) resulted in appearance a new band at 1710 cm^{-1} of acetone bonded by hydrogen bonding to Si–OH groups, some amount of which exists in silicalite. This last band shows a submaximum at 1695 cm^{-1}. This last band (1695 cm^{-1} one) is the main band in the spectrum of acetone adsorbed on SiO_2 (spectrum c), in which the concentration of surface Si–OH groups is very high. The hydrogen bonding of Si–OH groups with acetone is also well seen in the region of O–H vibrations (spectra not shown). The sorption of acetone in HZSM-5 zeolite containing both Si–OH and acidic Si–OH–Al groups (spectrum d) results in appearance similar bands as for SiO_2: 1710 and 1685 cm^{-1} but this last band shows a submaximum at low frequency side, which may be assigned to the hydrogen bonding of acetone with acidic Si–OH–Al.

According to the data presented in Fig. 1 (spectrum e), the sorption of acetone in CuZSM-5 resulted in appearance of

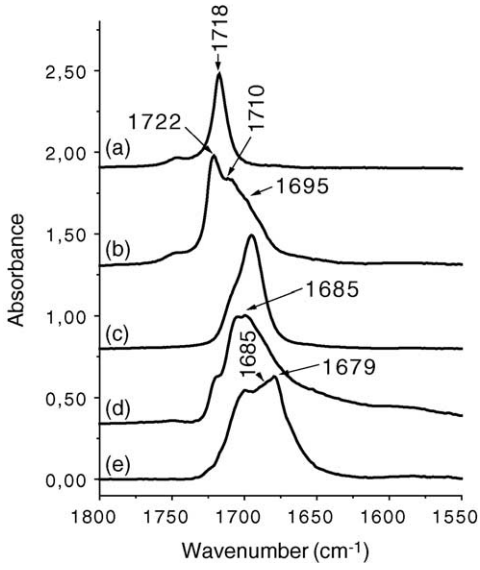

Fig. 1. IR spectra of acetone: at solution in CCl_4 (a), as well as adsorbed on silicalite (b), SiO_2 (c), zeolite HZSM-5 (d) and zeolite CuZSM-5 (e).

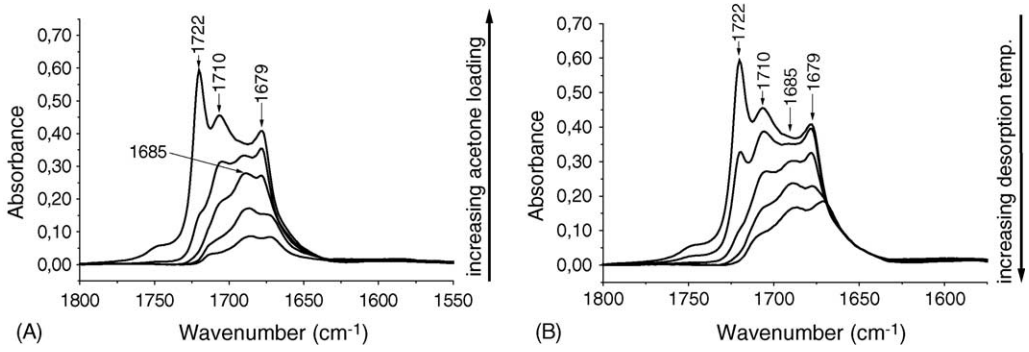

Fig. 2. IR spectra recorded upon the sorption of increasing amounts of acetone in CuZSM-5 (A) and desorption of acetone from CuZSM-5 at increasing temperatures (B).

all mentioned above bands of physisorbed and hydrogen-bonded acetone (1722–1685 cm^{-1}), as well as a new maximum at 1679 cm^{-1} which is absent in zeolites without Cu. This band can be assigned to acetone bonded to Cu^+.

The information on stability of acetone complexes bonded to OH groups and to Cu^+ ions was studied in the experiments in which the small doses of acetone were sorbed in CuZSM-5 as well as in desorption experiments. The results are presented in Fig. 2. The sorption of first doses of acetone (Fig. 2A) resulted in appearance of the bands of acetone bonded both to OH groups and to Cu^+ ions. At high loadings, the band of physisorbed acetone (1722 cm^{-1}) is present. The desorption at increasing temperatures (Fig. 2B) resulted in the decrease of all the acetone bands but the bands of physisorbed acetone (1722 cm^{-1}) and acetone bonded to OH groups (1710 and 1685 cm^{-1}) decreased at first, whereas the band of acetone bonded to Cu^+ (1679 cm^{-1}) remained even at high temperature. These results indicates that Cu^+ sites bond acetone more strongly than hydroxyl groups.

The spectra of acetone sorbed in CuMCM-41 are presented in Fig. 3. The results obtained for CuMCM-41 are similar as for CuZSM-5. Two bands are present at 1700 and 1677 cm^{-1} of acetone bonded to silanol groups and to Cu^+ cations. The bands assigned to acetone interacting with bridging hydroxyls which were present in the case of CuZSM-5 are absent if acetone was sorbed in CuMCM-41. The spectra recorded upon the sorption of increasing amounts of acetone in CuMCM-41 are presented in Fig. 3A. The first portions of acetone reacted with Cu^+ ions (the band 1677 cm^{-1}) whereas at high loadings it is bonded to silanol groups (band at 1700 cm^{-1}). The desorption of increasing temperatures (Fig. 3B) removed the molecules bonded to silanol groups in the first order and the molecule bonded to Cu^+ ions remained. These results evidence once more that (similarly as for CuZSM-5) acetone molecules are more strongly bonded to Cu^+ than to other adsorption sites.

The red shift of IR band of C=O interacting with Cu^+ by 39 cm^{-1} (CuZSM-5) or 41 cm^{-1} (CuMCM-41) indicates that the activation of C=O bond takes place. This phenomenon is similar as that observed in the case of alkenes. Most probably the activation of C=O bond is realized similarly as for alkenes by π back donation of d electrons of Cu^+ to antibonding π^* orbitals of acetone.

3.3. Interaction of acetone with Cu^+ sites in zeolites CuX and CuY

The spectra of CO groups in acetone sorbed in CuX and CuY are presented in Fig. 4. The bands at 1667 cm^{-1} (CuX, spectrum a) and 1669 cm^{-1} (CuY, spectrum b) can be assigned to CO in acetone interacting with Cu^+. The second intensive band at 1708–1712 cm^{-1} is characteristic for acetone interacting with Na^+ ions still present in both zeolites CuX and CuY ($\Delta\nu$ = 10 and 6 cm^{-1}, respectively).

The frequencies of the bands of acetone interacting with Cu^+ in CuX (1667 cm^{-1}) and CuY (1669 cm^{-1}) are lower than for CuZSM-5 (1679 cm^{-1}) and CuMCM-41 (1677 cm^{-1}). The sequence of the values of frequency shifts: CuZSM-5 (39 cm^{-1}) $\approx$ CuMCM-41 (41 cm^{-1}) $<$ CuY (49 cm^{-1}) $<$ CuX (51 cm^{-1}) may be related to the increasing amount of AlO_4^- tetrahedral in zeolite and to the increase of negative charge on oxygen atoms, and therefore to increase of neutralization effect of Cu^+ cation charge.

3.4. The effect of acetone sorption on framework vibration of CuZSM-5

The information on the interaction of zeolitic cations with adsorbed molecules can be also obtained by recording IR spectra in ‘‘transmission window’’, i.e. in spectral region 900–1000 cm^{-1}. This method was first suggested by Sarkany et al. [22–26] and next developed by other authors [27–30]. The spectra of CuZSM-5 at ‘‘transmission window’’ recorded at 170 K are presented in Fig. 5. Spectrum of activated zeolite (spectrum a) shows a band at 960 cm^{-1} of zeolitic oxygen rings deformed by the presence of Cu^+ cation inside the ring. The spectrum b was recorded upon the sorption of acetone at room temperature. The differential spectrum (c = b−a) shows the shift of 960 cm^{-1} band to lower frequency (towards the position of the band of

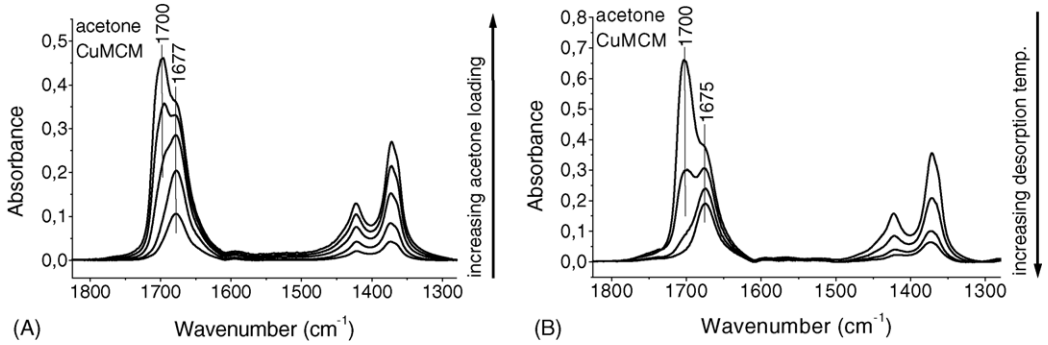

Fig. 3. IR spectra of acetone sorbed in CuX (A) and CuY (B).

unperturbed rings) by 26 cm^{-1}. The band shift indicates that the interaction of Cu^+ cation with acetone molecule results in withdrawing of the cation from the oxygen ring what results in some ring relaxation. Similar effects were obtained upon the adsorption of alkenes in CuZSM-5. The Δv value obtained for acetone (26 cm^{-1}) is distinctly higher than observed before for CO (7 cm^{-1} [26]) indicating much stronger interaction of Cu^+ with acetone than with CO but still smaller than for alkenes, such as but-1-ene or propene (36 cm^{-1} [11]).

3.5. The mechanism of acetone activation—DFT calculations

As mentioned, our calculations have been performed for a model of cationic copper site that was cut off the MFI structure taken from Accelryss databases included in the software. The basket (M7) model was composed of two fused 5T rings forming a 6T ring which simulated framework environment for copper cations in α-position on the main channel wall of MFI structure. This model has already been elaborated by us and studied in more detail previously [5–7]. The calculations evidenced that copper cation (Cu^+) was coordinated by four framework oxygen atoms with the following bond distances: 2.04, 2.05, 2.24, 2.43 Å (Fig. 6).

Earlier our study [11,12] showed that Cu^+ site activated alkenes significantly. An acetone molecule is slightly different from alkenes but still is a π-electron system. According to the results of our calculation, acetone adsorbed on the model of the copper cationic site (Fig. 7) with adsorption energy of 233 kJ/mol, which was more than that for strongly adsorbed alkenes (ca. 200 kJ/mol). The adsorption energy of acetone interacting with Cu^+ in zeolite was also higher than interacting with OH group in HZSM-5: experimental value 130 kJ/mol [18] and calculated value 139 kJ/mol [20]. Acetone molecule was found to be situated close to the copper site ($R_{Cu–O}$ = 1.87 A) and the interaction was significant. Although mainly the interaction between the adsorption center and the molecule is reproduced, significantly high calculated adsorption energy indicates that stabilizing effect of the framework is also included. The interaction with acetone resulted in breaking two bonds between framework oxygens and copper cation and finally copper cation was surrounded by three oxygen atoms: two oxygens from framework and one from carbonyl group of acetone. The withdrawing Cu^+ from the oxygen ring resulted in some ring relaxation. This is well seen in IR spectra presented in Fig. 5. The shift by 26 cm^{-1} of 960 cm^{-1} band of vibration of oxygen ring towards the position typical of unperturbed ring. According to the DFT calculations, the angle Cu–O–C equal to 150° indicated a slight distortion

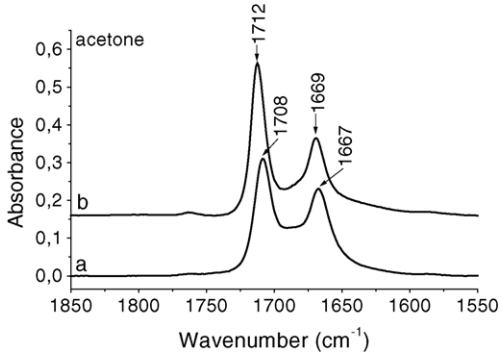

Fig. 4. IR spectra recorded upon the sorption of increasing amounts of acetone in CuMCM-41 (a) and desorption of acetone from MCM-41 at increasing temperatures (b).

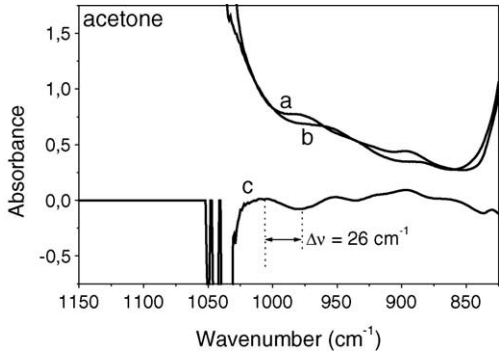

Fig. 5. The IR spectra of CuZSM-5 recorded (at 170 K) at ''transmission window'' upon the sorption of acetone. The spectra were recorded before (a) and after the sorption (b), differential spectrum c = b−a.

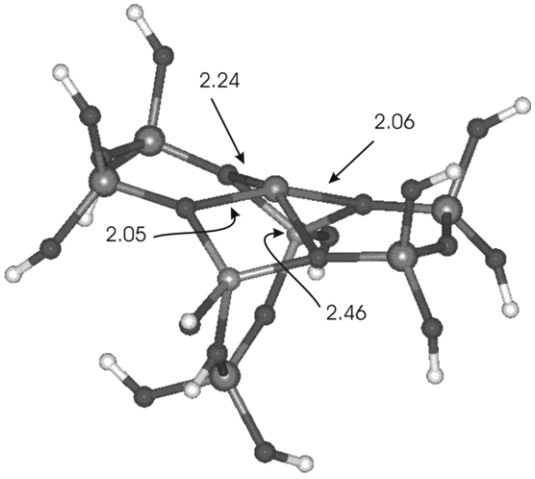

Fig. 6. The model of copper cationic site in zeolite ZSM-5.

from linear adsorption. Carbonyl bond (C=O) was lengthened by 0.0014 nm which is one-third of that for C=C bond in alkenes. The calculated red shift of carbonyl IR band by 61 cm^{-1} matched experimental value (39–51 cm^{-1}). This red shift was lower than that observed for alkenes (78–130 cm^{-1}). The significant difference of the activation reflected in electron structure of the adduct acetone–copper site. The activation of C=O bond (the C=O band shift is bigger than for acetone interacting with Na^+: 6–10 cm^{-1}, Fig. 5) may be the result of π back donation of d electrons of Cu^+ to the antibonding orbitals of molecule. However, other effect: the donation electron from the acetone molecule (most likely from lone electron pair of oxygen) to Cu^+ cation may also take place. Our calculation evidenced that the molecule of acetone became positive (+0.15) upon the adsorption. Therefore, the effective flow of electrons suggested that the donation effect from acetone to Cu^+ cation was more pronounced than π back donation from Cu^+ to acetone.

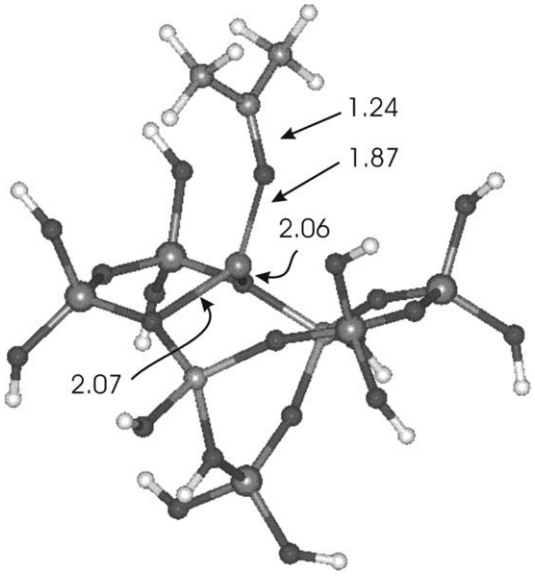

Fig. 7. The copper cationic site interacting with acetone molecule.

The information on the ability of molecule to give or take electrons can be obtained by considering the electron donor and acceptor properties of both molecules and adsorption site. The electron affinity (EA) determines π back donation ability of the molecule. The medium value of electron affinity for acetone (0.8 eV) implies its moderate ability of π back donation (i.e. of taking electrons). Acetone is better electron acceptor than alkenes (EA ca. 1.3 eV) while it is still worse than NO (EA = 0.5 eV). On the other hand, acetone has a relative high value of HOMO energy (−5.8 eV) if comparing with alkenes and acetylene (−6.5 to −7.5 eV). Acetone may be therefore not only good electron acceptor but even better electron donor. As mentioned our DFT calculations evidenced that the acetone molecule got positive charge when interacting with Cu^+ in zeolite, while Cu^+ did not change its charge (+0.32). Therefore, the charge distribution analysis indicates that the framework was beneficent of electrons. This is again a situation in which zeolite framework acts as a reservoir of electrons. In this case, however, the transition of electrons from acetone to framework via Cu^+ cation takes place. It was just the opposite as in the case of alkenes, the molecules of which became negative [10,12] and the transfer of electrons from both Cu^+ and framework to alkene molecules occurred.

Summarizing, the reactive adsorption of organic π-electron molecules on the cationic site leads to the flow of electrons which depends on electron donor/acceptor properties of both: the hosting site in a zeolite framework and the guest molecule. One of the indication of good electron donor ability is high HOMO energy. Electron accepting properties of a molecule can be estimated on the basis of electron affinity. The lower electron affinity the bigger electron accepting abilities, thus the bigger π back donation can be expected. Both these factors determine to what extent the molecule is activated.

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