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Characterization of the Cu^+ sites in MFI zeolites: combined computational and experimental study

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Abstract

The site-specificity of the CO probe molecule interaction with the Cu^+/MFI system is investigated by a combination of experimental and theoretical techniques. Three Cu^+ site types differing in CO adsorption energies (E_{ads}) were identified. Based on a very good agreement of experimental and calculated E_{ads}, the detail information about the structure and localization of Cu^+ sites in MFI, including information about the localization of framework Al atom can be obtained. The IR spectra of CO adsorbed on the same Cu^+/MFI samples clearly shows that the CO stretching frequencies are not site-specific in Cu^+/MFI system. This conclusion is supported by calculated CO frequencies that do not depend on the Cu^+ site type.

Keywords: Copper; Zeolite; MFI; Carbon monoxide; TPD; FT-IR

1. Introduction

Copper ions implanted in pentasil-ring zeolites have been recognized as promising catalysts for direct NO decomposition to molecular nitrogen and oxygen and selective catalytic reduction of NO with hydrocarbons [1–3]. The catalytic activity of copper ions substantially differs for various zeolite structures, Si/Al ratio, and Cu loading [3–6]. Therefore, great attention has been paid to characterization of the copper zeolite systems and to the elucidation of the structure and nature of active sites in these systems. Probe molecules (e.g. CO, N_2 or NO) are often used for Cu/zeolite characterization employing a variety of techniques, such as microcalorimetry, EPR, FT-IR, UV–vis–NIR, and EXAFS spectroscopy. These techniques brought indirect proofs that copper ions are coordinated in high-silica zeolites in several site types [7–13]. However, the interpretation of experimental data at the atomic scale level is not straightforward in many cases due to the lack of information about the framework aluminum distribution/localization and about the structure of active sites. One of the most important questions is whether a particular experimental technique can provide information about the details of Cu^+ coordination environment (site-specificity of the method).

The goal of the present study is to clarify which of the experimental technique employing the CO probe molecule is site-specific for the Cu^+/MFI system. FT-IR of adsorbed CO molecule was used in order to distinguish the various coordination types of extra-framework cations in Cu^+-zeolites. Rather different conclusions were drawn; while some authors concluded that a band at 2158 cm^{-1} can be deconvoluted into two peaks (2151 and 2159 cm^{-1}) and assigned them to different types of Cu^+ sites [10,13], others found that the Cu^+ site types cannot be distinguished from CO FT-IR spectra [11,12]. Based on the theoretical study, it was concluded that CO stretching frequencies are not site-specific for Cu^+/MFI system [14]. On the contrary, rather recent combined experimental and theoretical study of CO desorption from Cu^+/MFI showed that CO adsorption energies are site-specific [15]. Therefore, the interaction of CO molecules with Cu^+ sites in MFI was investigated by a

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combination of both FT-IR and TPD techniques on the same set of Cu^+/MFI samples. Experimental results were compared with the results of quantum chemical modeling of CO interaction with Cu^+ ions at different sites in MFI.

2. Experiment

The samples of CuNa–MFI zeolites with Si/Al ratio 14.1 were prepared by the ion-exchange process from Na–MFI parent zeolite [4]. The chemical composition was determined by WD-XRF spectroscopy and samples were labeled as CuNa–MFI-*X* (*X* stands for Cu/Al ratio). For FT-IR studies, the zeolites were pressed into thin self-supporting wafers (thickness 7–10 mg/cm^2). The samples were activated in situ in an IR cell under vacuum or 80 Torr of CO at 480 °C overnight. Activated samples were saturated by 25 Torr of CO at RT and subsequently, evacuated for 30 min at different temperatures from RT to 450 °C. IR spectra were recorded with resolution 0.5 cm^{-1} using an FT-IR spectrometer Nicolet Protege 460 equipped by MCT/B detector. Hundred milligrams of CuNa–MFI zeolite was used for each TPD experiment. Prior to the TPD experiment, samples were reduced for 1 h at 500 °C in the flow of CO/He mixture containing 5 vol.% of CO and then saturated by CO at RT for 1 h. CO-TPD experiments were carried out in the temperature range from 25 to 600 °C with the heating rate 10 °C/min. The CO desorption was monitored by OmniStar GSD 300 quadrupole mass spectrometer. More details about TPD experiment can be found in Ref. [15].

The formal kinetics-based model was used for modelling of the CO-TPD spectra. The desorption and readsorption processes were described by the first- and second-order kinetic equations, respectively, and Arrhenius expression was adopted for the rate constants. The population of the Cu^+ sites, frequency factors and desorption energies for all sites were optimized to obtain the best fit with the experimental data. All experimental spectra were fitted at once constraining the kinetic parameters to be the same for all samples [15].

3. Calculations

The interaction of CO molecules with the Cu^+ ions in the vicinity of a single framework Al atom on the channel intersection (eight sites, Al atom at T1, T2, T3, T5, T6, T7, T9, and T12 positions) and on the channel wall (four sites, Al atom at T4, T8, T10, and T11), and in the vicinity of a pair of framework Al atoms (various placement of Al pair within M6 site [16]) was investigated using combined quantum mechanics/interatomic potential function method (QM-pot) [17]. At this level of theory the part of the system, inner part (CO, Cu^+, and framework atoms in the vicinity of CO–Cu^+), was described at the DFT level and the rest of the zeolite was described with interatomic potential function (for details see Ref. [14]). Adsorption energies were calculated with the B3LYP exchange correlation functional [18]. The CO stretching vibrations were obtained from scaling method based on the correlation of ν(CO) calculated at highly reliable CCSD(T) method and r(CO) optimized at DFT level. This scaling method does not depend on the exchange-correlation functional [14], thus, the BLYP functional [19,20] and large inner part size definition (up to 23 framework T atoms) was used. A counterpoise correction method was used for the basis set superposition error (BSSE) evaluation [21] and zero-point-vibrational energy (ZPE) was accounted for within the harmonic approximation. QM-Pot, Turbomol, GULP, and Gaussian 03 program packages were used [22–25].

4. Results

The TPD curves for CuNa–MFI zeolites with various copper contents are presented in Fig. 1A. All CO-TPD

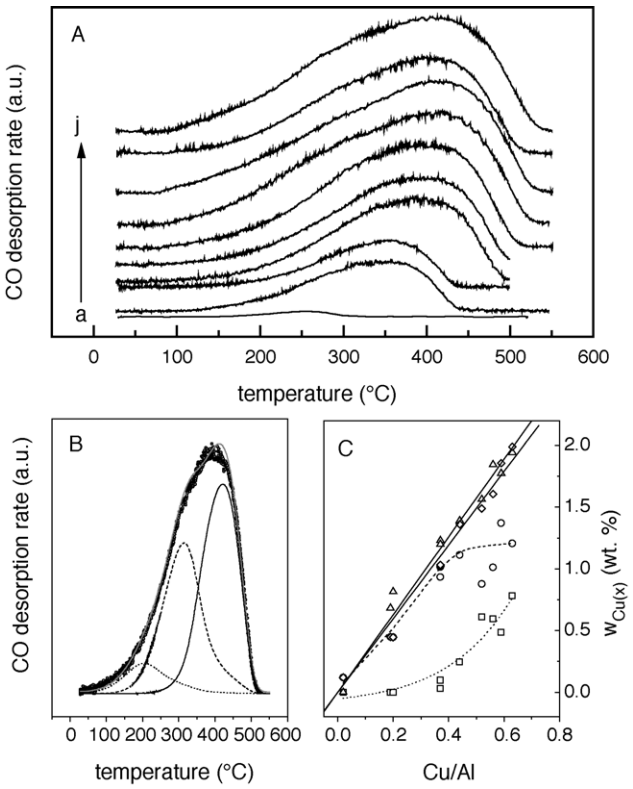

Fig. 1. (A) CO-TPD desorption spectra obtained for CuNa–MFI zeolites with different Cu/Al ratio: a 0.02; b 0.19; c 0.20; d 0.37; e 0.37; f 0.44; g 0.52; h 0.56; i 0.59; and j 0.63. (B) Experimental and simulated CO-TPD spectra of CuNa–MFI-0.44 zeolite, (○) experimental data; gray line: simulated TPD curve; (—) desorption peak with desorption energy 121.8 kJ/mol; (- - - -) desorption peak with desorption energy 96.7 kJ/mol; and (···) desorption peak with desorption energy 77.0 kJ/mol. (C) The population of the Cu^+ site types for CuNa–MFI zeolites with increasing copper loading obtained from CO-TPD simulation. (□) Cu sites with CO desorption energy 77.0 kJ/mol; (○) Cu sites with CO desorption energy 96.7 kJ/mol; (Δ) Cu sites with CO desorption energy 121.8 kJ/mol; and (◇) sum of Cu sites with desorption energies 96.7 and 77.0 kJ/mol.

spectra exhibit a single very broad and asymmetrical peak at 50–540 °C, with a maximum shifting to higher temperatures with increasing copper content. This suggests heterogeneity of Cu^+ sites and/or very intensive readsorption of carbon monoxide. Total amount of desorbed CO calculated from TPD spectra is proportional to copper content. Quantitative analysis led to conclusion that TPD experiments start from materials where each Cu^+ site bonds one molecule of carbon monoxide, and adsorption of CO on Na^+ sites does not occur. Amount of desorbed CO molecules from fully oxidized and fully reduced samples was negligible. The spectra for parent Na-zeolite and for Cu^{2+}- and Cu^0-zeolites are not shown.

The proposed kinetic model of CO desorption is capable to describe the experimental TPD data when the existence of three Cu^+ site types with different CO adsorption energies is assumed. Fitted TPD spectra give for individual Cu^+ sites desorption energies: 77.0, 96.7 and 121.8 kJ/mol. An example of experimental and simulated curves together with individual desorption peaks attributed to individual Cu^+ desorption sites is presented in Fig. 1B. The TPD spectra analysis led to conclusion that relative population of the particular Cu^+ sites depends on the copper content in the zeolite (see Fig. 1C). The numbers of sites with the highest desorption energy linearly increases with the Cu/Al ratio. The population of sites with desorption energy of 96.7 kJ/mol increases with copper content up to Cu/Al = 0.5 and then it levels-off, while the sites with the lowest desorption energy are populated for samples with Cu/Al > 0.35.

The character of the Cu^+ sites was investigated also by means of IR spectroscopy. Spectra of monocarbonyls species for the CuNa–MFI zeolites with different Cu loading are depicted in Fig. 2A. Assuming that the CO stretching frequency is site-specific, the spectra obtained for samples with various Cu loading should be different. However, the spectra exhibit single bands at 2158 cm^{-1} and the shape of the adsorption band is nearly the same (as can be seen from the normalized spectra in Fig. 2B). The effect of the coverage changes (reached by partial desorption of CO) at different temperatures) was investigated for CuNa–MFI-0.19 sample reduced in the CO atmosphere at 480 °C overnight. Intensity of the absorption band rapidly decreased with increasing temperature of the evacuation (see Fig. 2C). However, the small amount of carbonyls is stable even under evacuation at 300 °C for 30 min. It is likely that the spectra taken upon the evacuation at 300 °C are dominated by CO adsorbed on the Cu^+ site with largest desorption energy 121.8 kJ/mol, while the spectra obtained after evacuation at RT are due to CO adsorbed at all three types of adsorption sites. From the normalized spectra (Fig. 2D), it is evident that all spectra have a band with the same shape and maximum at 2158 cm^{-1}. It can be concluded that the CO stretching frequency is not site-specific in Cu^+/MFI.

The calculated CO stretching frequencies for Cu^+ sites on the channel wall (type I, Fig. 3A) and for intersection Cu^+ sites (type II, Fig. 3B) are in the range 2159–2170 and 2159–2164 cm^{-1}, respectively, in very good agreement with

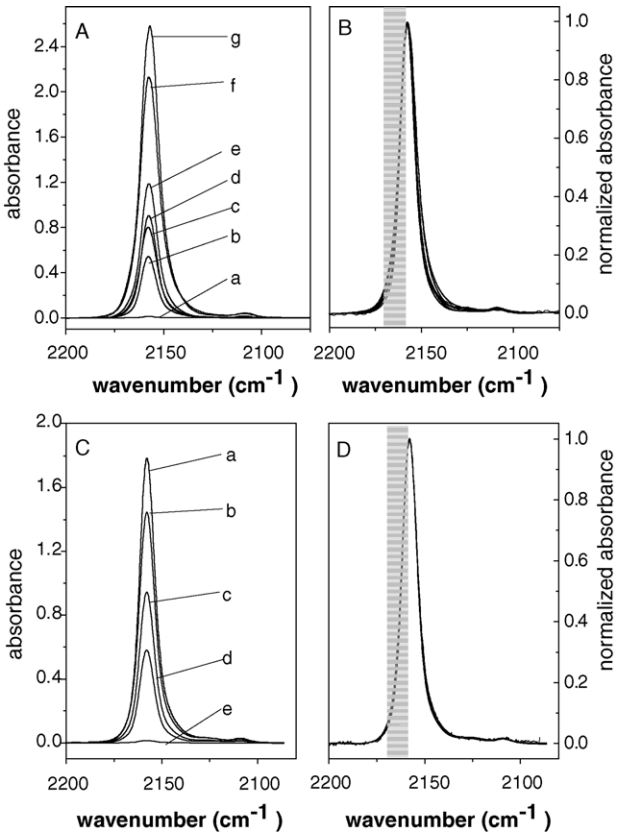

Fig. 2. (A) The IR spectra of CO adsorbed at RT on CuNa–MFI zeolites with Si/Al 14.1 and various Cu/Al ratio reduced in vacuum at 480 °C. Twenty-five Torr of CO was adsorbed on the samples for 1 h and subsequently evacuated at RT for 30 min. a 0.02; b 0.19; c 0.29; d 0.37; e 0.44; f 0.52; and g 0.63. (B) The IR spectra from Fig. 1A normalized to height of band at 2158 cm^{-1}. Shaded rectangle depicts the range of calculated CO stretching frequencies. (C) The IR spectra of the CO molecules adsorbed on CuNa–MFI-0.19 reduced in the 80 Torr CO at 480 °C overnight. Twenty-five Torr CO was adsorbed on the sample at RT and evacuated at different temperatures for 30 min. a RT; b 100 °C; c 150 °C; d 200 °C; and e 300 °C. (D) The IR spectra from Fig. 1C normalized to height of band at 2158 cm^{-1}. Shaded rectangle depicts the range of calculated CO stretching frequencies.

experimental spectra (Fig. 2). No correlation between the Cu^+ site type and ν(CO) and no correlation between the calculated CO adsorption energies and ν(CO) was found. Thus, precise calculations of ν(CO) support the conclusion of experimental study that the CO stretching frequencies are not site-specific in Cu^+/MFI system. The calculated CO adsorption energies for sites on the intersection, on the channel wall, and sites in the vicinity of two framework Al atoms (134, 108, and 84 kJ/mol) are in good agreement with the desorption energies obtained from the fit of experimental TPD spectra. Based on the agreement of experimental and calculated adsorption energies, the particular site type obtained from TPD analysis can be linked with particular site type from quantum chemical calculations: (i) the strongest interaction of CO with Cu^+ is found for sites on the channel intersection (122 kJ/mol) where Cu^+ is originally coordinated to just two framework oxygen atoms of single AlO_4 tetrahedron (Fig. 3B). These sites are dominantly

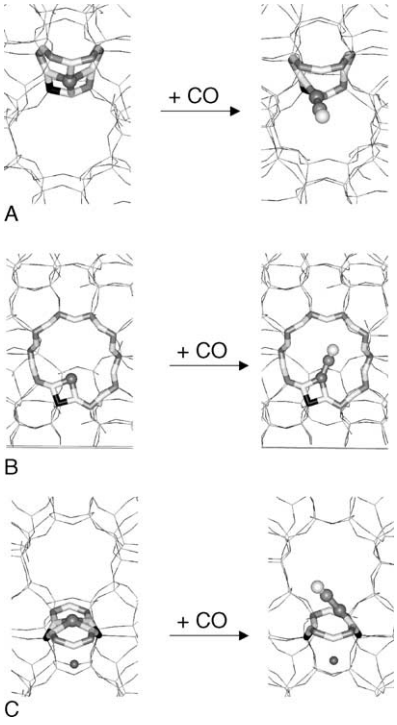

Fig. 3. Coordination and localization of Cu^+ ions in MFI with and without adsorbed CO molecule. Oxygen and aluminum atoms depicted in white and black, respectively. Cu atom and CO molecules depicted as balls. (A) The Cu^+ site on the channel wall (type I site, Al at T10) populated when framework Al atom is in T4, T8, T10, or T11 position. (B) The Cu^+ site on the channel intersection (type II site, Al at T12) populated when framework Al atom is in T1, T2, T3, T5, T6, T7, T9, or T12 position. (C) The Cu^+ site in the vicinity of framework Al pair. Symmetrical arrangement of Al atom within the M6 site (see Ref. [28] for details) is depicted.

populated when framework Al atom is located on the edge of the channel intersection [16]. (ii) The interaction of CO with Cu^+ sites on the channel wall, where Cu^+ is originally coordinated to three–four framework oxygen atoms of six-member ring on the channel wall (Fig. 3A), is about 25 kJ/mol weaker. These Cu^+ sites are populated when framework Al atom is in T4, T8, T10, and T11 positions. (iii) The CO interaction with the Cu^+ sites on the six-member ring with two framework Al atoms (Fig. 3C) is weakest (77 kJ/mol). Our results based on TPD curve fitting and on QM-Pot calculations are in good agreement with microcalorimetric experiments (−130 [26], −100 and −121 kJ/mol [27]).

Upon the interaction with CO, the Cu^+ ion stays coordinated to only two framework O atoms of single AlO_4 tetrahedron (Fig. 3). Regardless of the Cu^+ coordination to the framework before interaction with CO, the Cu^+–CO complex has very similar structure for all sites considered. As a consequence, the CO frequencies are the same for all Cu^+ site types. On the contrary, E_{des} is smaller for Cu^+ sites on the channel wall than for sites on the channel intersection. In order to bind CO efficiently, the Cu^+ ions at the channel wall sites need to reduce coordination with the framework. The ''deformation'' energy associated with the coordination reduction is responsible for small E_{ads} on Cu^+ at channel wall sites. We suggest that this observation is rather general for small probe molecules interacting with metal ion sites in zeolites: techniques that probe interaction energy are more likely to be site-specific than techniques probing the structure or dynamics of adsorbed complex.

5. Conclusion

The interaction of CO with the Cu^+ sites in MFI was investigated by a combination of experimental and theoretical techniques. It is shown that desorption energies of CO from Cu^+/MFI are site-specific. Three types of Cu^+ sites in MFI can be distinguished from TPD spectra: (i) Cu^+ sites on the channel intersection (E_{des} = 122 kJ/mol), (ii) Cu^+ sites on the channel wall (E_{des} = 97 kJ/mol), and (iii) Cu^+ sites on the channel wall in the vicinity of two framework Al atoms (E_{des} = 77 kJ/mol). Very good agreement between experimentally observed and calculated desorption energies was found. The IR spectra of CO adsorbed on the same Cu^+/MFI samples were measured. It is clear that the CO stretching frequencies are not site-specific in investigated Cu^+/MFI systems. The same conclusion can be drawn based on the calculated CO frequencies for various Cu^+ sites in zeolites that are in excellent agreement with experimental data.

The combination of experimental and theoretical description of CO/Cu^+/MFI system brings detailed information about the structure and localization of Cu^+ sites in MFI. In addition, from the population of individual Cu^+ site types, information about the framework Al atom localization is obtained.

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