Characterization of the $\text{Cu}^+$ sites in high-silica zeolites interacting with CO molecule: combined computational and experimental study.

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Introduction

Characterization of the copper/zeolite systems attracts a large attention of both experimentalists and theoreticians. Knowledge about the details of the structure and coordination of copper ions in high-silica zeolites is essential for understanding the mechanism of deNO$_x$ processes at the atomic scale level.

Often the CO molecule was used as a probe in characterization of the Cu$^+$ sites in zeolites.\textsuperscript{(1-3)} CO strongly interacts with Cu$^+$ ions inside the zeolite matrix forming mono-, di-, and even tri-carbonyl species.\textsuperscript{(1)} IR bands in the range 2129-2164 cm$^{-1}$ (2157-2159 cm$^{-1}$ for MFI) were assigned to CO stretching mode of mono-carbonyl. Some authors deconvoluted this band into two peaks (2151 and 2159 cm$^{-1}$ for MFI) and assigned them to different Cu$^+$ sites.\textsuperscript{(2)} CO stretching band observed for Cu$^+$/zeolite systems is blue-shifted with respect to the frequency of CO in the gas phase.

The interaction of copper ions with MFI and FER frameworks was studied previously in our laboratory by means of the combined QM-pot technique.\textsuperscript{(4,5)} Two dominant types of the Cu$^+$ ion sites were identified in both zeolite frameworks. Sites where the Cu$^+$ ions are coordinated to 3 or 4 oxygen atoms of six-membered ring on the wall of one of the channels are denoted “type I” sites. Site where the Cu$^+$ ions are coordinated to only two oxygen atoms of the AlO$_4$ tetrahedron located on the channel intersection are denoted “type II” sites.

Results and Discussion

In this contribution we present the results of the combined quantum mechanical/interatomic potential function (QM-pot)\textsuperscript{(6)} study of the CO interaction with copper sites in high-silica zeolites (MFI and FER) together with TPD and FTIR spectra of CO adsorbed in various high-silica zeolite matrices.

The results of the combined QM-pot study show that two different Cu$^+$ site types identified in high-silica zeolite matrices become very similar upon the interaction with the single molecule of carbon monoxide. The overall coordination number for Cu$^+$ is 3 (2 framework oxygen atoms and a carbon atom of CO) for all structures considered. The geometrical parameters and vibrational frequencies are also very similar for both Cu$^+$ site types. The CO adsorption energies are larger on the sites on the intersection than on the sites on the channel wall. For the Cu$^+$ sites on the intersection there is almost no change in the coordination of the Cu$^+$ ions with the
zeolite framework upon the interaction with CO. On the contrary, for the Cu$^+$ sites on
the channel wall the Cu$^+$ ion loses partially its coordination with the zeolite
framework upon the interaction with CO. Partial loss of the Cu$^+$ coordination
-corresponds to the smaller adsorption energies of CO at these sites. In order to bind
CO efficiently the Cu$^+$ ion must be lifted farther from the channel wall, thus,
decreasing the Cu$^+$…zeolite framework interaction. Calculated differences in CO
adsorption energies are in good agreement with available experimental data and with
the results of TPD study. There are only small differences between the Cu$^+$ sites on
the channel intersection of MFI and FER. However, the sites on the channel wall of
MFI and FER differ by almost 10 kcal/mol in CO interaction energies. The
interaction energy of CO with the Cu$^+$ sites is smaller when Cu$^+$ is located on top of
the six membered ring consisting of two AlO$_4$ tetrahedra.

The CO stretching frequencies calculated for CO bound at type I and type II sites of
Cu$^+$ in MFI are both in the same range. Therefore, based on the results of QM-pot
study the two types of Cu$^+$ sites in MFI could not be distinguished by CO stretching
frequency. On the contrary, the computed CO stretching frequencies for CO on type I
sites (channel wall) of Cu$^+$/FER are about 10 cm$^{-1}$ larger than those for type II sites.
Therefore, we carried out a series of FTIR measurements of CO stretching
frequencies for MFI and FER samples for various temperatures. For MFI we found
that normalized bands do not change their shape with increasing temperature, while
for FER we found that the band shape changes with the increasing temperature (the
-intensity of lower frequency band increases with the increasing temperature). These
experimental and theoretical results are in very good agreement.

References
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