The Impact of Finite Temperature on the Coordination of Cu Cations in the Zeolite SSZ-13

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Abstract

Understanding the fundamental properties of the Cu-exchanged zeolite SSZ-13, a catalyst for the selective catalytic reduction of nitrous oxides in the presence of ammonia, is a major challenge. Recent results for vibrational spectroscopy show that the active Cu centers are not static at room temperature, but change their coordination regularly when probe molecules are adsorbed. In this work we model the movement of bare Cu cations in SSZ-13 at room temperature (300K) using ab-initio molecular dynamics simulations. We find that Cu cations also change their coordination without adsorbent. We identify different coordinations for different oxidation states and analyze their distribution in dependence on the local Al position. The results in this work show that this thermal motion of the cation is a general feature, which probably influences the interpretation of various characterization methods as well as reaction path analysis. In the future it will be interesting to see which conditions have to be fulfilled that similar phenomena can also be observed for other systems.

Keywords: Cu-SSZ13, Ab-Initio molecular dynamics, zeolite structures, selective catalytic reduction

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1. Introduction

Nitrous oxides (NO_x) are created in the combustion of fossil fuels and are major environmental pollutants. The growing awareness of their negative implications such as in acid rain has led to a more strict emission legislation over recent years and has made the catalytic removal of NO_x a major challenge in the automotive industry. Many different possible pathways to achieve that goal exist, but today it seems like the selective catalytic reduction of NO_x in the presence of ammonia using small pore, Cu-exchanged zeolites[1, 2] represents the economically most feasible option. This is due to the excellent performance of the catalyst over the full range of reaction conditions encountered[3, 4] as well as its high hydrothermal stability[5], which prevents the loss of activity during the harsh conditions upon catalyst regeneration.

While the favorable properties of Cu-SSZ-13, a zeolite in the chabazite structure, have been discovered several years ago[1, 4, 5], it is still not fully understood how this catalyst works. The first complication is the characterization of the active sites. Initial XRD measurements revealed that the active sites are located in the six-membered ring of the zeolite[2, 6]. However, these measurements were performed in zeolites with an Si/Al ratio of about 6. More recent studies for catalysts with Si/Al ratios above 12 revealed, that Cu atoms forming Cu-OH complexes are located in the eight membered rings of the SSZ-13 structure[7, 8]. This suggests a connection between the nature of the active centers and the presence of Al atoms in the framework.

A method that is sensitive to differences in the local chemical environment of these sites is vibrational spectroscopy of adsorbed tracer molecules such as CO and NO[9, 10]. Comparing experimental measurements to theoretical calculations allows the assignment of certain spectroscopic features to an atomistic structure of the Cu site[11, 12, 8, 13]. Zhang et al. performed a very detailed study for NO adsorption and found a highly complex Cu(II)-NO spectrum, which could not fully be explained using static density functional theory calculations[8], a point that caught our attention.

We studied this Cu(II)-NO feature under the following assumptions[13]: (i) a distribution of different local Al positions is present in the realistic material, (ii) based upon thermodynamics the most stable Cu positions will be occupied first and (iii) it is necessary to model the system under the encountered conditions, i.e. introducing finite temperature using molecular dynamics simulations. Following this approach we found that even though

the cations are still located either in the six- or eight-membered rings, finite temperature leads to changes in their local coordination, which in turn leads to complex multi peak spectra for single adsorbed NO molecules to single active sites. Using these spectra we were finally able to closely reproduce the experimentally observed spectra.

These results clearly violate the standard paradigm that one active site with one adsorbed molecule only leads to one peak, but open at the same time the question about circumstances required to observe such behavior. Additionally it is a quite interesting question, whether this thermal motion is only present in spectroscopy or whether it also influences specific reaction intermediates and pathways[14, 15, 16].

In this work we therefore study the thermal motion of different Cu(I) and Cu(II) centers in SSZ-13 at room temperature (300K) using molecular dynamics simulations. We find that the coordination of Cu centers changes for both oxidation states an effect that is more pronounced for Cu^I . These results imply that it is necessary to include finite temperature effects for reaction intermediates and characterization techniques, a feature that will significantly influence our understanding of the reaction pathway and fundamental materials properties.

2. The System

In this work we investigate Cu-exchanged SSZ-13, a zeolite in the chabazite structure[17] (see (a) in Fig. 1). The minimal unit cell contains 12 tetrahedral sites (T-sites). All T-sites are symmetrically equivalent and in the neutral framework they are only occupied with Si atoms. The framework is activated by the presence of Al atoms, which are not able to fully saturate the bonds to the four surrounding O atoms and are therefore associated with a negative charge. The amount of Al atoms in the framework is given by the Si/Al ratio. However, based on experimentally observed Si/Al ratios there is not always an integer number of Al atoms present in one unit cell[9, 6, 7, 18, 19, 8]. Therefore a distribution of local Al configurations, similar to defects in metals or metal oxides, will be present. To take this into account we will study all possible configurations for one, two and three Al atoms in the unit cell (see (b) in Fig. 1).

The negative charge associated with the Al atoms is compensated by the presence of a Cu counteranion. In Cu-SSZ-13 oxidation states of +1 (Cu^I) and +2 (Cu^{II}) are observed. Each Cu^I cation is associated with one Al atom,

Figure 1: In this work we study Cu sites in SSZ-13. SSZ-13 is a zeolite in the chabazite framework (displayed in (a)), the zeolite structure with the most simple primitive unit cell. Yellow atoms correspond to Si, red atoms to O and the primitive unit cell is displayed. (b) We perform calculations for all different possibilities to distribute one, two or three Al atoms in one unit cell. The double six-ring structure of the unit cell is displayed schematically and red dots correspond to the positions of Al atoms.

each Cu^{II} cation with two Al atoms. To compensate the presence of additional Al atoms we add a proton in the energetically most favorable position. Additionally we form the Cu^{II} cation in the unit cell with only one Al by the addition of OH. This situation corresponds to a large separation between Al atoms, where the charge of the Cu^{II} -cation cannot be compensated locally by Al. Careful calculations reveal that the bare cations are always most stable in the six-ring, while the Cu-OH site is most stable in the eight-ring[17, 12, 13].

3. Results

In this work we perform molecular dynamics simulations at room temperature (300 K). At these conditions, typically encountered in characterization studies, we find a distribution of different cation coordinations for all Al positions. We also find these coordinations as stable local minima at 0 K. However, without thermal motion only the thermodynamic minimum will be accessible. At finite temperature some of these minima become accessible and, as discussed below, a distribution of them is present. Identifying the different configurations based upon geometric data in the trajectories is not always straightforward, since the bond-lengths oscillate around a minimum. We will therefore discuss the applied criteria for identification of the configurations in the appropriate spots in the text.

3.1. Cu^I

As already mentioned above, we investigated sites where the monovalent Cu atom is located in the six membered ring, but Al atoms are in different positions. However, for all 10 different possibilities we basically find three different Cu-configurations displayed in Fig. 2. In the first case (Cu^I -A in Fig. 2) the Cu-cation is located in the center of the six-ring and forms strong bonds (most of the time shorter than 2.3 Å) to every other O atom in the ring. In the other two possibilities only two strong bonds and one significantly weaker bond are formed. In one of those two cases (Cu^I -B in Fig. 2) the Cu-atom forms strong bonds to two O atoms, separated by one O-atom, to which the Cu is weakly bonded to. In the other case (Cu^I -C in 2) the Cu-atom is bonded to O atoms on opposite sides of the six ring and the weak bond is formed to one of the other O-atoms.

When analyzing the MD trajectories we find transitions on a one ps timescale between these three possibilities. For further analysis it is therefore necessary to define guidelines, when a given configuration is encountered.

Figure 2: At finite temperature we find different coordinations of Cu^{I} sites. All three possibilities are shown here. We only show the six-ring containing the Cu atom with one possible Al position. Si atoms are shown in yellow, O atoms in red, Al atoms in grey and Cu atoms in blue.

The most obvious distinction is between configurations A and B on one side and configuration C on the other side. If the two O atoms, where the Cu atom is strongly bonded to, are only separated by one O atom it corresponds to either configuration A or B, if not it corresponds to configuration C. We furthermore define the system to be in configuration A, if the distance to the O atom on the other side of the ring is shorter than the distance to the O atom located between the two O atoms Cu is strongly bonded to.

The distribution of the Al atoms in the six ring influences the encountered configurations in two ways, namely (i) the bonds to the activated O atoms (O atoms next to Al atoms) are slightly shorter and more difficult to break and (ii) the Al-O bonds are longer than Si-O bonds, leading to a different local strain, which again influences the coupling between the lattice vibrations and the Cu-motion. Therefore the occupation of the different configurations are quite different for different Al positions in the unit cell.

The different occupations of the configurations are shown in Fig. 3. Most often either $\text{Cu}^I\text{-A}$ or $\text{Cu}^I\text{-B}$ is occupied. For four of the 10 Al positions we find that the system is more than 95% of the time in one of the configurations (three times $\text{Cu}^I\text{-A}$ and one time $\text{Cu}^I\text{-B}$) and in one case $\text{Cu}^I\text{-A}$ and in one other case $\text{Cu}^I\text{-B}$ is occupied more than 80% of the time. For the remaining four cases the system switches between two or three possible configurations. In addition it is important to notice that only for one of all Al positions $\text{Cu}^I\text{-C}$ is occupied more than 10% of the time, while its presence is almost negligible (<2%) for most of the other cases.

A last observation was that breaking the bonds to non-activated O atoms (i.e. O atoms next to Si atoms), which causes a transition between configurations A and B, is on a one ps timescale. However, in some rare cases we also find the breaking of activated bonds. We see a maximum of two of those events in our 70 ps simulation time. Therefore it is a rare event in those timescales and arriving at fully ergodic results goes far beyond the simulation times studied here and would probably require more advanced simulation techniques.

3.2. Cu^{II}

The situation changes quite significantly when Cu^{II} is considered. Compared to monovalent Cu, which is mainly ionically bound to the framework, the opening of the d-shell in the divalent cation leads to a significant covalent contribution in bonding. This generally results in a few changes in the bonding, i.e. the coordination number is slightly higher (3-4 compared to 2-3 in

Figure 3: The distribution of Cu^I -coordinations for different Al positions in the unit cell observed in molecular dynamics simulations over 70 ps. The pie diagrams use the color code of the frames in Fig. 2, with blue corresponding to site Cu^I -A, brown for Cu^I -B and yellow to Cu^I -C. For almost all Al positions the Cu atom moves between different coordinations, which we attribute to the ionic nature of the bond between Cu and zeolite.

the Cu(I) case), the bonds are on average shorter and the bonding to especially the activated O-atoms leads to a larger strain on the T-sites. All these points have already been discussed in the literature[17], but it is unclear how it affects the dynamical behavior of those sites at finite temperature.

The stronger bonding to the framework actually prevents the fast bond breaking encountered in the Cu^I case. Again we find different local Cu configurations for the sites, where the Cu is positioned in the six ring (see Fig. 4). For Cu^{II} we find four different configurations. In the first one (Cu^{II} -A in Fig. 4) the Cu-cation is again positioned close to the center of the six ring. However, now it is fourfold coordinated. The other three configurations are encountered when one of the bonds is broken. In one case it leads to a configuration very similar to Cu^I -A with three strong bonds (Cu^{II} -B in Fig. 4), while for another configuration (Cu^{II} -C in Fig. 4) three strong bonds to neighboring O atoms are formed. The last configuration (Cu^{II} -D in Fig. 4) is similar to Cu^I -C, again with three strong bonds. In the analysis we assume a bond to be broken if it is longer than 2.5 Å.

Most of the time Cu^{II} appears in configuration Cu^{II} -A (see Fig. 5). For five of these Al distributions the system is found in this configuration for more than 99.5% of the time. In all these situations two or three Al atoms are present in the same six-ring. Cu^{II} -A remains the main configuration for all the other Al distributions as well. For the remaining cases where two Al atoms are in the same six ring small occupations (<10%) of Cu^{II} -D and Cu^{II} -C is found. At the same time the latter of those sites is the second most likely if only one Al atom is in the same six ring (with occupations between 1.4% and 12.4%), with very small (<1%) Cu^{II} -B also present. It is also important to point out that none of these configurations is found for times longer than one or two ps.

The Cu-OH group is always twofold coordinated to the framework. Similar to the case of NO adsorption, here the movement is mainly in the movement of the OH-group. It is composed of a rotation but we also observe a translation within the unit cell. However, it is very difficult to present quantitative statistics in this case.

4. Discussion

The results presented in this work show that the motion of Cu cations cannot be neglected at finite temperature. We modeled this system at room temperature, but it can be expected that the effect is even larger at higher

Figure 4: For Cu^{II} we find four different possibly coordinations. While some of them are very similar to Cu^I (see Fig. 2, Cu^{II} binds in general more strongly to the framework, which on average leads to a higher coordination number and shorter bonds. The color code corresponds to Fig. 2.

Figure 5: The distribution of Cu^{II} -coordinations for different Al positions in the unit cell observed in molecular dynamics simulations over 70 ps. The pie diagrams use the color code of the frames of Fig. 4, with blue corresponding to site Cu^{II} -A, green to Cu^{II} -B, yellow to Cu^{II} -C and orange to Cu^{II} -D. For all Al positions Cu is most often in the Cu^{II} -A coordination. This is due to the stronger interactions between Cu^{II} and the framework, which leads to smaller movement of the atom.

temperatures. We find that the changes in coordination are far more significant for the monovalent cations. This is not surprising, since this cation has a fully filled d-shell, which leads to a mainly ionic bond between Cu and the framework. As soon as the d-shell is opened, bonding has a strong covalent component, which leads to a much weaker dynamical behavior.

The results in this work show that this change in coordination found in previous work for NO adsorbed to Cu^{II} sites in SSZ-13 seems to be a more general feature of Cu-sites in the material and influences the interpretation of experimental data and could influence the calculation of reaction paths in various ways. First of all, the cation motion has to be taken into account for various characterization techniques. As already discussed for vibrational spectra, one local Al distribution possibly leads to a set of signals for the different coordinations encountered, due to the thermal motion. This effect is larger for Cu^I , but at the same time not negligible for Cu^{II} . A possible solution to this problem is to perform measurements at low temperature. This should reduce the thermal motion and lead to results that are more easily interpreted. However, depending on the characterization technique this might lead to other complications, such as the adsorption of multiple probe molecules in vibrational spectroscopy[10].

At the same time, the results presented in this study are also important for reaction path analysis. Different studies have tried to identify reaction pathways for deNO_x -SCR using static electronic structure calculations[15, 16]. In these studies it is assumed that it is the redox properties of Cu, i.e. switching between +1 and +2 oxidation states, that play a key role for the high catalytic activity of this material. However, based on this work thermal motion will also play a significant role, especially for the Cu^I intermediates at reaction temperatures above room temperature. Due to the changes in electronic structure enthalpy barriers are most likely different for the different Cu-coordinations, but more importantly, changes in the entropy contributions can be expected.

5. Conclusion

In this work we modeled the thermal motion of Cu^I and Cu^{II} cations for different Al distributions in the zeolite SSZ-13 using molecular dynamics simulations. We find that the local coordination of the Cu cations changes significantly and that Cu moves between different coordinations for most of the Al-distributions. This movement is larger for Cu^I , which, compared to

Cu^{II} , is more weakly bound to the framework. The phenomena discussed in this work impact the interpretation of various characterization methods, as well as reaction path analysis. In the future it will be interesting to see whether these effects can also be observed for different metal sites on different supports and what conditions need to be fulfilled to observe such a behavior.

6. Theoretical Methods

All calculations were carried out using the Vienna Ab-Initio Simulation Package (VASP)[20, 21], a plane-wave code using PAW pseudopotentials[22]. The energy cut off for the basis set was set to 420 eV and k-point sampling was restricted to the Γ -point. Electron-electron interactions in ab-initio molecular dynamics simulations were described using density functional theory’s generalized gradient approximation in the parameterization of Perdew, Burke and Ernzerhof (PBE)[23]. After an initial equilibration of the system we performed 140000 steps at a timestep of 0.5 fs (total sampling time 70 ps) for all sites. Similar time intervals were shown to lead to ergodic results for NO adsorbed to Cu^{II} centers in zeolites. To arrive at a canonical ensemble at 300K we used a Langevin thermostat with stochastic boundary conditions[24, 13]. The corresponding trajectories were evaluated using an adapted version of FlexMD[26]. Geometric parameters of the unit cell were chosen similar to previous studies[17, 25, 11] and the volume was fixed to 830 Å³.

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***Graphical Abstract (for review)**