

# Cu Exchange and Siting Preference in Zeolites: the Influence of the framework topology

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## Abstract

Cu-exchange SSZ-13 has been confirmed active for the selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> in diesel engine aftertreatment system. The nature of the Cu siting in the SSZ-13 is essential to the redox cycle and the Cu pairability. However, SSZ-13 is a zeolite material with Chabazite topology, which contains only one symmetry-distinct tetrahedral-site and 3-dimensional pore openings. The influence of the zeolite topology in the Cu exchange is still unclear. In this work, we performed Plane-wave-based Density Functional Theory supercell calculations to investigate the Cu exchange and siting preference in 4 different frameworks. We choose FER, AEI and TON to be compared with CHA to address different features of the framework topology including the pore dimensionality, the number of distinct T-site, the double-six-ring building unit, etc. Our results show the similarity and difference between zeolite frameworks

## Introduction

### Objectives

We compare the types of Cu sites and exchange energetics, compositional phase diagrams among CHA, AEI, FER and TON in order to 1) understand the influence of zeolite topology, similarities and differences between different framework. 2) Propose a design strategy to guide the choice of zeolite framework to achieve specific catalytic purposes.

### Justification

1. Cu SSZ-13 is a ion-exchange zeolite material that has a chabazite framework. implemented as the on-board selective catalytic reduction (SCR)

catalysts in diesel engine aftertreatment system. The whole SCR cycle include the pairing and oxidation of 2 Cu<sup>+</sup> clusters to a Cu<sup>2+</sup> oxo cluster, and the reduction of the Cu<sup>2+</sup> back to Cu<sup>+</sup>. Thus, the nature of the Cu<sup>+</sup> and Cu<sup>2+</sup> are essential to learn the relation between the SCR mechanism and the framework topology, Si/Al ratio, etc.

1. In SSZ-13 it is now well established that Cu<sup>2+</sup> exchanges into the framework at proximal pairs of charge-compensating framework Al within a six-membered ring (6MR) to create Z2Cu sites and at isolated framework Al to form ZCu<sub>2+</sub>OH sites. [5] Experiments and calculations are consistent with preferential population of the former sites before the latter. By combining this insight with models for the distribution of Al on the SSZ-13 framework, it is possible to create a composition phase diagram for relative fractions of Z2Cu and ZCuOH in SSZ-13. [5]
1. Construction of the composition phase diagram for SSZ-13 is facilitated by the high symmetry of the CHA lattice, resulting in only one symmetry-distinct tetrahedral site. In this work, we explore extending this methodology to lower symmetry frameworks, with a particular emphasis on AEI, FER and TON, chosen because they represent different numbers of symmetry-distinct T-site, different pore dimensionality, different building units.

## Background

1. SSZ-13 is on-board catalyst for SCR

Zeolite, a type of mesoporous aluminosilicate materials, are mainly used as catalyst in petroleum engineering or oil refining reactions. Cu-exchange SSZ-13 draws attention in the past decades for being used as the on-board catalyst for selective catalytic reduction (SCR) of NO<sub>X</sub> with NH<sub>3</sub>. [3–5] It is a type of zeolite that has chabazite topology with Cu exchanged as extraframework counter-ions.

2. The Cu exchange and siting have been investigated both experimentally and theoretically

The SCR process involves the pairing of Cu<sup>1+</sup> to form Cu oxo clusters, and the reduction of Cu<sup>2+</sup>. [4] Thus, the Cu speciation and citing preferences

determines the performance of the SCR for the catalyst. In addition, Cu speciation also determines the hydrothermal stability of the catalyst, and the Cu citing is to a large degree dependent on the Al locations or the Al proximity in the zeolite. [2,5] Both experimental and computational methods have been implemented to learn the Cu speciation and siting preference in Cu-SSZ-13. Experimentally, polynuclear Cu<sup>2+</sup> species can be characterized by UV-vis and time-dependent DFT. [1]

### 3. Other emerging frameworks for SCR, and the uncertainty of the zeolite topology

The theoretical evaluation of Cu-SSZ-13 is facilitated by the fact that SSZ-13 is CHA topology with only 1 symmetry-distinct T-site.

### 4. Our approach in this paper

## Computational Methods

CHA, FER, AEI and TON conventional unit cells were determined from the IZA structure. A  $1 \times 1 \times 1$  supercell was constructed for CHA, FER and AEI, while a  $1 \times 1 \times 2$  supercell was constructed for TON. For each framework, Si was substituted by Al to cover all available T-sites. H, Cu and CuOH were placed in all possible locations in each T-site for each framework. A enumeration code was established to enumerate all possible T-site pairs for each framework, and 2 Si were substituted by Al. DFT simulations were performed using the Vienna ab-initio Simulation Package (VASP). Spin-polarized DFT energies were determined within the generalized gradient approximation and projector-augmented wave description of core states. Calculations are conducted with a 72 T-site supercell. Construction of relative energy diagrams followed the previous procedures [5] and was further normalized to mole of exchanged Cu ions.

## Guidance to the reader

Here, we compute the DFT exchange energies for Z<sub>2</sub>Cu and ZCuOH in CHA, AEI, FER and TON. We build a linear model to .....

## Results and Discussions

### Sites in CHA, AEI, FER and TON

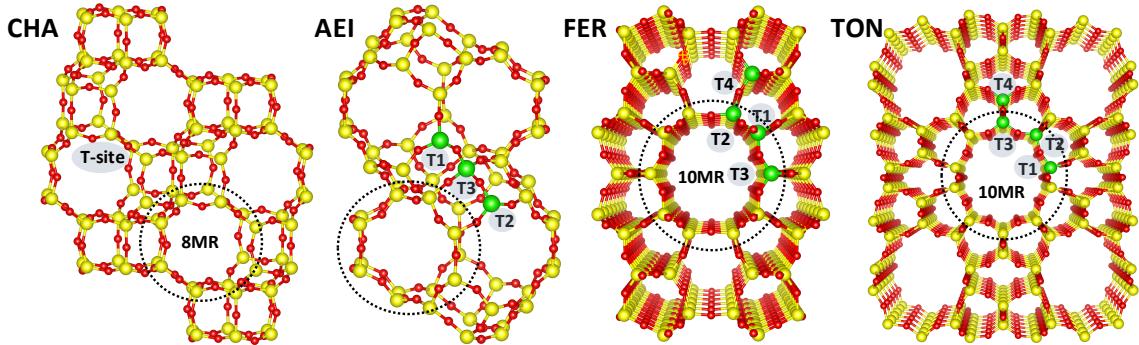


Figure 1: Demonstrations of zeolite frameworks, T-site types for CHA, AEI, FER and TON. CHA and AEI show cage-shaped structures, and FER, TON show channel-shaped structures. Due to the space limitation, the channel in 1 dimension is drawn in FER.

1. CHA and AEI have three-dimensional window structure formed from 8-membered-ring, but a different stacking of the double 6-ring building units(Figure 1a, 1b). The resulting cages for CHA and AEI have oblate and pear-shaped cavities. FER has a two-dimensional window structure formed from both 10- and 8-membered-ring channels (Figure 1c), and TON has a one-dimensional window structure formed from 10-membered-ring channels (Figure 1d). The consequence of different dimensional window structure is some isolated or paired Al sites are blocked by small-number-ring walls to electrostatically tether Cu ions.
2. CHA has only one symmetry-distinct tetrahedral-site (T-site) (Figure 1a), while AEI has 3 symmetry-distinct T-sites (Figure 1b). Both FER and TON have 4 symmetry-distinct T-sites (Figure 1c, 1d). The numbering of different T sites are also labeled in Figure 1. Those 3 types of T-sites in AEI all have a multiplicity of 16 in a 48 T-site conventional AEI unit cell. T1, T2, T3 and T4 sites in FER have multiplicities of 16, 8, 8 and 4 in a 36 T-site conventional unit cell. TON has multiplicities of 8, 8, 4 and 4 for T1 to T4 sites in a 24 T-site conventional unit cell. The T4 site in TON is inaccessible to the large 10-membered-ring pore openings, resulting in different Cu ion exchange properties.

- When Cu is exchanged in the framework, it maintains either +1 or +2 state, which resulting in ZCu, ZCuOH and Z<sub>2</sub>Cu forms. Here, Z indicates a framework Al site. These sites form in exchange with the bronsted-acid sites (ZH and Z<sub>2</sub>H<sub>2</sub>) that are pre-existed in the framework.
- The types of isolated proton and isolated Cu energies are the same to the types of symmetry-distinct T-sites in all zeolite frameworks. For the types of Z<sub>2</sub>H<sub>2</sub> and Z<sub>2</sub>Cu sites, we used a previously developed enumeration code to identify the Al proximity in 4 zeolite frameworks. [5] The unique Al pairs are classified as "clusters" in the enumeration code, and the identified unique Al clusters, which will be included in subsequent paired Al exchange energy analysis.

### Isolated Al exchange energies

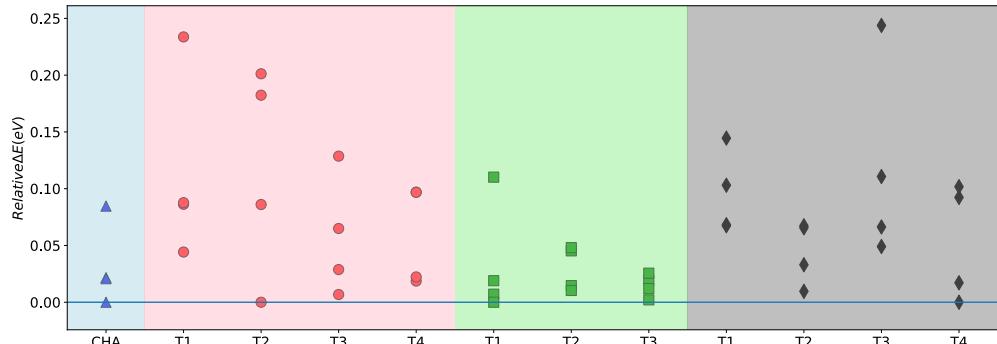


Figure 2: ZH exchange energies for CHA, AEI, FER and TON. Energies are normalized to the lowest energy for each T site.

- We picked up each framework, placed proton close to all possible 4 neighboring oxygen atoms for each T-site, and did DFT optimizations. In Figure 2, the DFT energies of ZH for all symmetry-distinct T-sites in CHA, AEI, FER and TON are plotted relative to the lowest energy for each T-site in each framework. We The optimized structures of some particular interesting points are also plotted as inserted.
- For both CHA and AEI, The energies for 4 ZH locations in each T-site are comparable to one another. All proton are pointing into the nearby

large 8MR pore openings. The exceptions that draws our attention is the forth one in CHA and AEI T1.

### ZCuOH relative to CHA

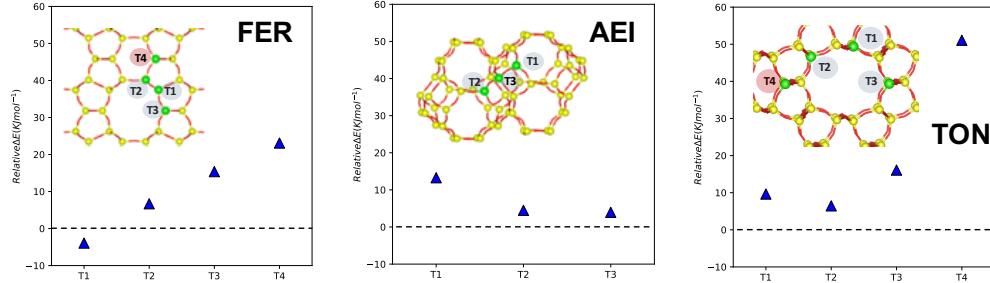


Figure 3: Relative ZCuOH exchange energies for (), (), () compared to CHA.

### Z2Cu relative to CHA

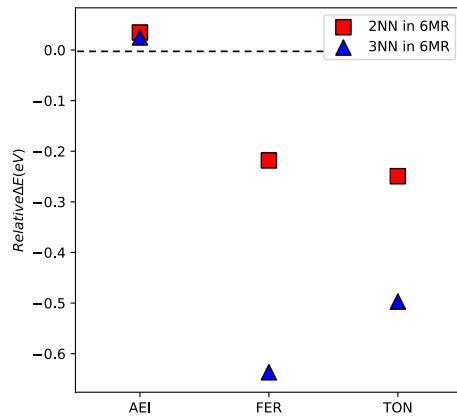


Figure 4: Z2Cu exchange energies relative to CHA for (), ( ), ( ), ( )

## Z<sub>2</sub>Cu to ZCuOH

### Compositional phase diagram

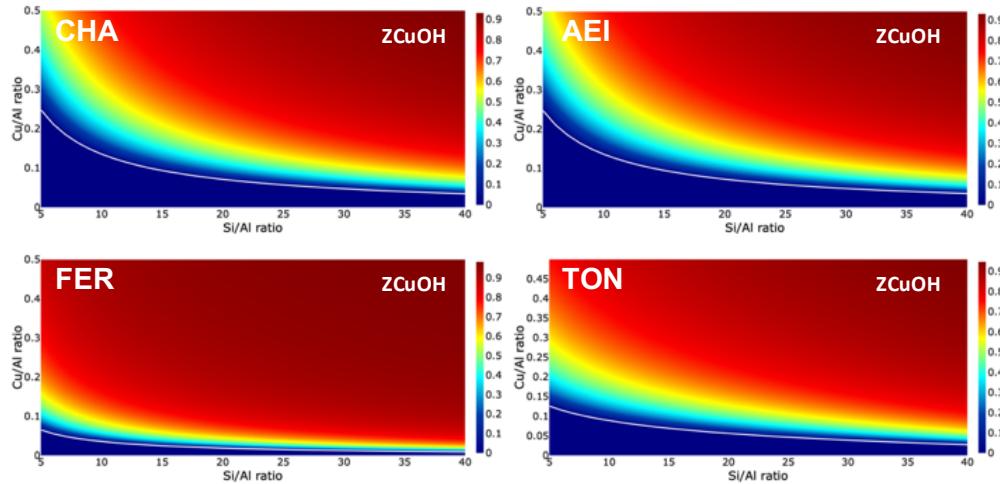


Figure 5: Compositional phase diagrams for (CHA), (AEI), (FER), (TON)

### Fitting models

### Conclusions

In this work, we interrogate and compare Cu ion exchange and siting preference in CHA, AEI, FER and TON zeolites through DFT supercell simulation, and identify the sensitivity of the Cu<sub>+</sub> and Cu<sub>2+</sub> to the zeolite topology, which promises the potential of rational choice of zeolite topology to tailor the Cu siting during SCR cycle. This work can be extended to predict the Cu siting of all 237 zeolite topologies for specific Cu ion properties of interest.

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