

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_x with NH₃ 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⁺ clusters to a Cu²⁺ oxo cluster, and the reduction of the Cu²⁺ back to Cu⁺. Thus, the nature of the Cu⁺ and Cu²⁺ are essential to learn the relation between the SCR mechanism and the framework topology, Si/Al ratio, etc.

2. In SSZ-13 it is now well established that Cu²⁺ 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 ZCu²⁺OH sites. [6] 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. [6]
3. 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_X with NH₃. [4–7] 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 Cu¹⁺ to form Cu oxo clusters, and the reduction of Cu²⁺. [5] 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. [3,6] Both experimental and computational methods have been implemented to learn the Cu speciation and siting preference in Cu-SSZ-13. Experimentally, polynuclear Cu²⁺ species can be characterized by UV-vis and time-dependent DFT. [2]

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

While the analysis of Cu-SSZ-13 is facilitated by the fact that SSZ-13 has CHA topology with only 1 symmetry-distinct T-site, there are other zeolite materials showing potential utilization as SCR catalyst including the state of art Fe-ZSM-5. [1] Recently, Cu-FER was also evaluated as SCR catalyst with NH₃ by H₂-TPR and FT-IR. [9] Cu-FER show better stability than Cu-MOR, which is another Cu-zeolite material. [8]

4. Our approach in this paper

In this work, we extend the evaluation of Cu speciation and siting preference to less symmetrical zeolite frameworks. We choose AEI, FER, TON along with CHA as representative topologies, because they have different number of symmetry-dinstinct T-site, and different dimensionality for the pore openings. We performed supercell-based DFT calculations, statistical enumeration to seek the similarity and difference of Cu speciation and siting preferences for those zeolites. We also build a model using machine learning regression to correlate the Cu exchange energies to the topological features. With our model, rational choice of zeolite framework is feasible to meet the specific requirement in Cu speciation and siting.

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 [6] and was further normalized to mole of exchanged Cu ions.

Results and Disscussions

Sites in CHA, AEI, FER and TON

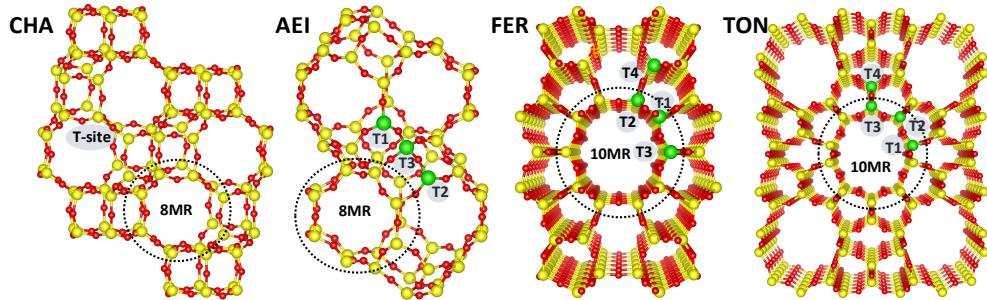


Figure 1: Demonstrations of zeolite frameworks, T-site types for CHA, AEI, FER and TON. CHA and AEI show cage-shaped structures, and FER, TON show channel-shaped structures. Due to the space limitation, the channel in 1 dimension is drawn in FER.

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.

3. When Cu is exchanged in the framework, it maintains either +1 or +2 state, which resulting in ZCu, ZCuOH and Z₂Cu forms. Here, Z indicates a framework Al site. These sites form in exchange with the bronsted-acid sites (ZH and Z₂H₂) that are pre-existed in the framework.
4. 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 Z₂H₂ and Z₂Cu sites, we used a previously developed enumeration code to identify the Al proximity in 4 zeolite frameworks. [6] 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

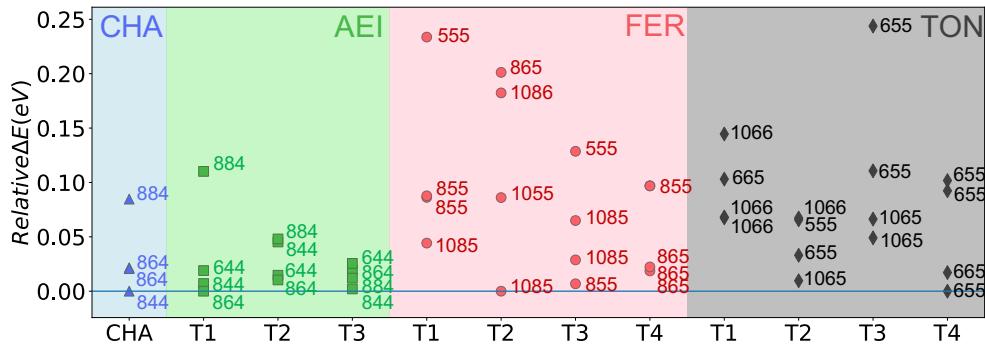


Figure 2: ZH exchange energies for CHA, AEI, FER and TON. Energies are normalized to the lowest energy for each framework.

1. 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 used a 3-digit notation to illustrate the local configuration of the ZH structure. For instance, "864" means the proton connects to 1 8MR, 1 6MR and 1 4MR nearby. The optimized structures of all ZH structures will be provided as CONTCAR format in the SI.
2. 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 draw our attention is the forth one in CHA and AEI T1. Those 2 points indicate the 884 ZH energies are much higher than other configurations, which is consistent with previous theoretical work reported for CHA.Li2018JPCC
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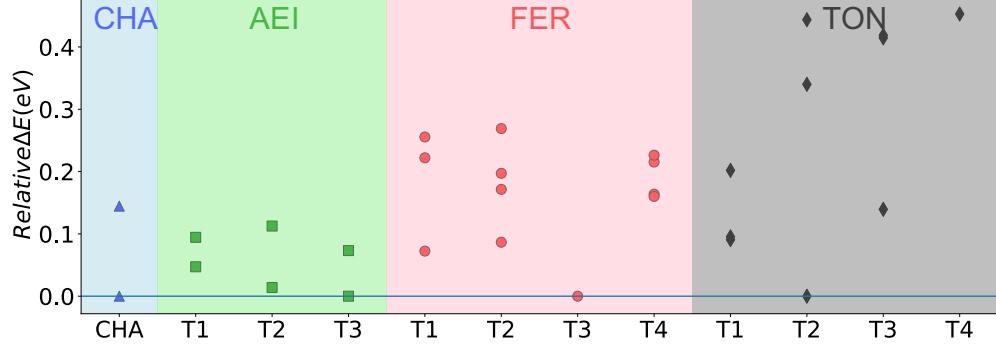


Figure 3: ZCuOH exchange energies for CHA, AEI, FER and TON. Energies are normalized to the lowest energy for each framework.

ZCuOH relative to CHA

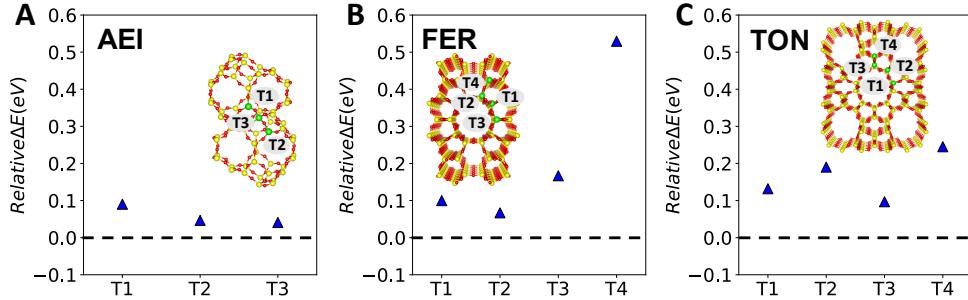


Figure 4: Relative ZCuOH exchange energies for ((), ((), () compared to CHA.

Z₂Cu relative to CHA

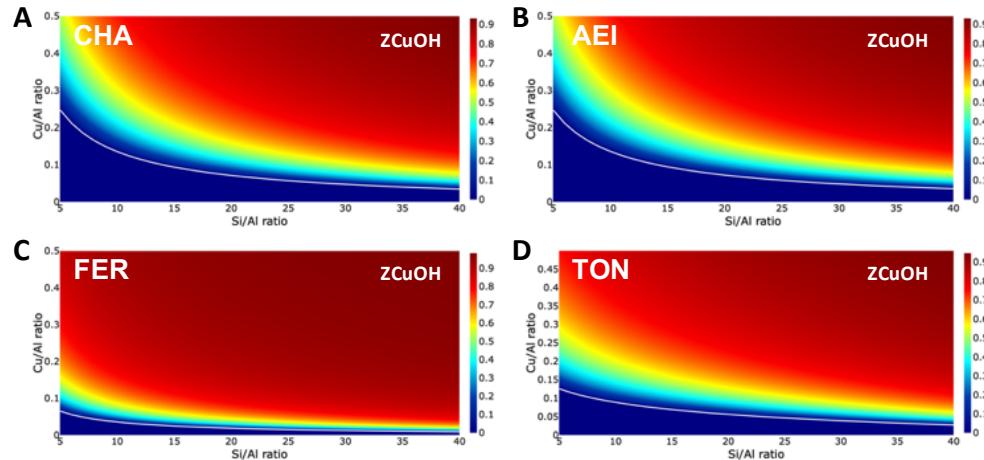


Figure 5: Z₂Cu exchange energies relative to CHA for ((), ((), ()

Z₂Cu to ZCuOH

Compositional phase diagram

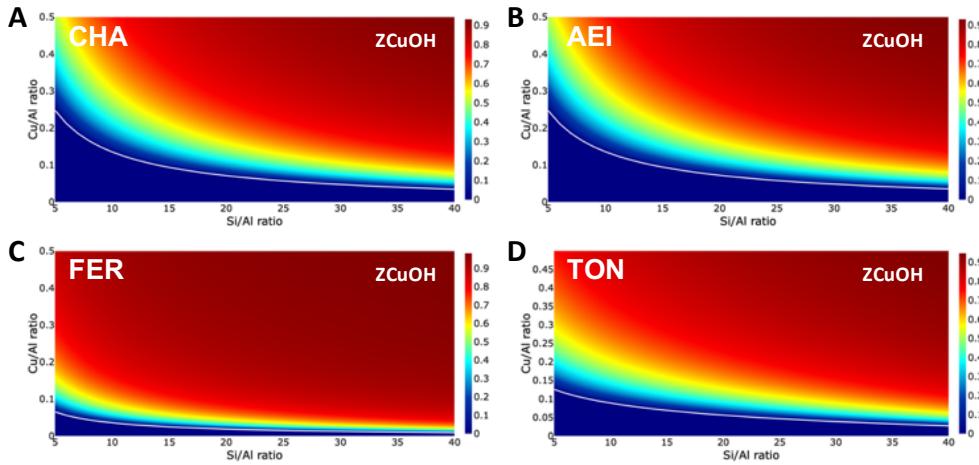


Figure 6: Compositional phase diagrams for (A), (B), (C), (D)

1. Based on the DFT energies, we found the

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₊ and Cu₂₊ 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.

References

- [1] Sandro Brandenberger, Oliver Kröcher, Arno Tissler, and Roderik Althoff. The state of the art in selective catalytic reduction of nox by ammonia using metal-exchanged zeolite catalysts. *Catalysis Reviews*, 50(4):492–531, 2008.

- [2] Hui Li, Christopher Paolucci, Ishant Khurana, Laura N. Wilcox, Florian Görtl, Jonatan D. Albarracin-Caballero, Arthur J. Shih, Fabio H. Ribeiro, Rajamani Gounder, and William F. Schneider. Consequences of exchange-site heterogeneity and dynamics on the UV-visible spectrum of Cu-exchanged SSZ-13. *Chemical Science*, 10(8):2373–2384, 2019.
- [3] Sichi Li, Hui Li, Rajamani Gounder, Anthony Debellis, Imke B Mu, Subramanian Prasad, Ahmad Moini, and William F Schneider. First-Principles Comparison of Proton and Divalent Copper Cation Exchange Energy Landscapes in SSZ-13 Zeolite. *Journal of Physical Chemistry C*, 122:23564–23573, 2018.
- [4] C. Paolucci, J. R. Di Iorio, F. H. Ribeiro, R. Gounder, and W. F. Schneider. *Catalysis Science of NO_x Selective Catalytic Reduction With Ammonia Over Cu-SSZ-13 and Cu-SAPO-34*, volume 59. Elsevier Inc., 1 edition, 2016.
- [5] Christopher Paolucci, Ishant Khurana, Atish A Parekh, Sichi Li, Arthur J Shih, Hui Li, John R Di Iorio, Jonatan D Albarracin-caballero, Aleksey Yezerets, Jeffrey T Miller, W Nicholas Delgass, Fabio H Ribeiro, William F Schneider, and Rajamani Gounder. Dynamic multinuclear sites formed by mobilized copper ions in NO_x selective catalytic reduction. *Science*, 357:898–903, 2017.
- [6] Christopher Paolucci, Atish A. Parekh, Ishant Khurana, John R. Di Iorio, Hui Li, Jonatan D. Albarracin Caballero, Arthur J. Shih, Trunojoyo Anggara, W. Nicholas Delgass, Jeffrey T. Miller, Fabio H. Ribeiro, Rajamani Gounder, and William F. Schneider. Catalysis in a cage: Condition-dependent speciation and dynamics of exchanged cu cations in ssz-13 zeolites. *Journal of the American Chemical Society*, 138(18):6028–6048, 2016.
- [7] Christopher Paolucci, Anuj A. Verma, Shane A. Bates, Vincent F. Kisper-sky, Jeffrey T. Miller, Rajamani Gounder, W. Nicholas Delgass, Fabio H. Ribeiro, and William F. Schneider. Isolation of the copper redox steps in the standard selective catalytic reduction on Cu-SSZ-13. *Angewandte Chemie - International Edition*, 53(44):11828–11833, 2014.
- [8] Asima Sultana, Tetsuya Nanba, Motoi Sasaki, Masaaki Haneda, Kunio Suzuki, and Hideaki Hamada. Selective catalytic reduction of nox with

- nh₃ over different copper exchanged zeolites in the presence of decane. *Catalysis today*, 164(1):495–499, 2011.
- [9] Marie-Laure Tarot, Mathias Barreau, Daniel Duprez, Vincent Lauga, Eduard Emil Iojoiu, Xavier Courtois, and Fabien Can. Influence of the sodium impregnation solvent on the deactivation of cu/fer-exchanged zeolites dedicated to the scr of nox with nh₃. *Catalysts*, 8(1):3, 2018.