

TRACKING THE ACTIVE COPPER SITES IN A CATALYTIC MINERAL

When copper ions exchange into a zeolite, the mineral becomes catalytically active for the selective reduction of nitrogen oxides, which are harmful gaseous environmental pollutants found in engine exhaust, into benign nitrogen. Copper-loaded zeolite catalysts are currently in commercial use on diesel vehicles, but many questions remain about the interplay between the composition of the zeolite, the reaction conditions, the active sites, and the catalytic mechanism. To understand zeolite dynamics, researchers performed *operando* x-ray absorption spectroscopy (XAS) experiments on Cu-zeolites under reaction conditions at the MR-CAT insertion device and bending magnet beamlines at the APS and correlated the results with first-principles simulations. The findings reveal the importance of reaction conditions to the active site properties and structure, providing critical insight that is needed to tune catalytic activity.

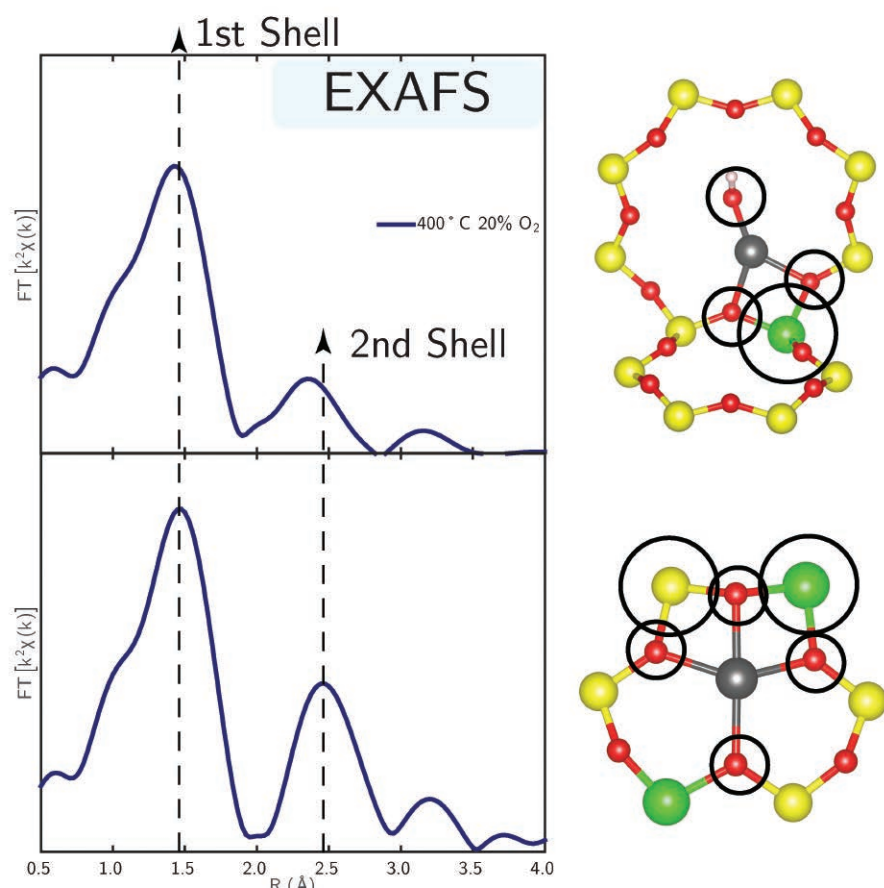


Fig. 1. EXAFS spectra and corresponding first-principles models distinguish two structural types of zeolite-supported Cu^{II} ions.

The particular zeolite of interest is SSZ-13, a nanoporous aluminosilicate constructed of 4-, 6-, and 8-membered rings of silicon, aluminum, and oxygen atoms. Copper ions associate with the framework aluminum centers. The structure of Cu depends on the number and arrangement of aluminum within the lattice and the oxidation state of the copper ions, among other factors. To determine the relationship between composition, structure, and catalytic function, the researchers synthesized and characterized zeolites with a range of elemental composition. They used the XAS technique at the MR-CAT 10-ID-B and 10-BM-A,B beamlines to measure the oxidation state of the copper species and evaluate their local geometric and electronic structures, as a function of the zeolite compositions. Complementary x-ray absorption near edge absorption (XANES) data, also collected at the MR-CAT beamline, was used to assess the copper oxidation state. The researchers identified and enumerated two types of aluminum sites within the zeolite that determine the Cu active site structure: the 1Al site, a six-membered ring with one aluminum atom and five silicon atoms, and the 2Al site, a six-membered ring with two aluminum atoms and four silicon.

Next, the researchers loaded copper ions into the zeolites and, again with XAS and XANES, studied how these metal ions embedded themselves into the zeolite mineral. They found that the copper atoms preferred exchanging at the 2Al site, where they took the form of Cu^{II} ions to exchanging at the 1Al site, where they exchanged in the Cu^{II}OH state. To assess the effect of environmental conditions on the Cu oxidation state and coordination environment, the researchers ran a series of first-principles simulations at varying conditions, including temperature, pressure, and reactant chemical potential.

The researchers compared these data to those collected experimentally, and found quantitative agreement.

To assess zeolite behavior in a real-world scenario, the researchers next studied "Copper" *cont'd. on page 100*

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copper speciation under the same working conditions used to catalyze the reduction of nitrogen oxide species. They used a custom-built reactor at the APS designed to collect XAS spectra under catalytic conditions, with the goal of determining the oxidation state of copper sites during the selective catalytic reaction of NO with ammonia to N₂. Again, the researchers performed simulations under the same set of conditions for comparison. The structure and dynamics of the copper ions were found to depend strongly on the reaction environment. For example, Cu ions are solvated by water at ambient conditions, but the hydration is lost at higher temperatures. Cu ions are also solvated by NH₃ under NO reduction conditions, which importantly cause mobilization of copper ions within the zeolite framework.

Together, the experimental data and simulations were used to develop a self-consistent picture of the reaction mechanism on copper ions in different local zeolite environments. Overall turnover rates and activation energies of the NO reduction reactions were similar on isolated Cu ions, regardless of zeolite framework. These findings have implications for the other chemistries catalyzed by Cu ions exchanged in zeolites, including the partial oxidation of methane, a process that may someday be harnessed by scientists to generate chemicals and fuels from abundant raw materials. —

Erika Gebel Berg

See: Christopher Paolucci¹, Atish A. Parekh², Ishant Khurana², John R. Dilorio², Hui Li¹, Jonatan D. Albarracin Caballero², Arthur J. Shih², Trunojoyo Anggara¹, W. Nicholas Delgass², Jeffrey T. Miller², Fabio H. Ribeiro², Rajamani Gounder², and William F. Schneider^{1*}, “Catalysis in a Cage: Condition-Dependent Speciation and Dynamics of Exchanged Cu Cations in SSZ-13 Zeolites,” *J. Am. Chem. Soc.* **138**, 6028 (2016).

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Author affiliations: ¹University of Notre Dame, ²Purdue University

Correspondence: * wschneider@nd.edu

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