

# Nature of Active Sites in Cu-exchanged small pore zeolites during NH<sub>3</sub>-SCR: An *operando* X-ray Absorption Spectroscopy Study

Rachit Khare<sup>1\*</sup>, Mirjam Wenig<sup>1</sup>, Andreas Jentys<sup>1</sup>, Johannes A. Lercher<sup>1</sup>

<sup>1</sup>Department of Chemistry and Catalysis Research Center, Technical University of Munich, Garching 85748 (Germany)

\*rachit.khare@tum.de

## Introduction

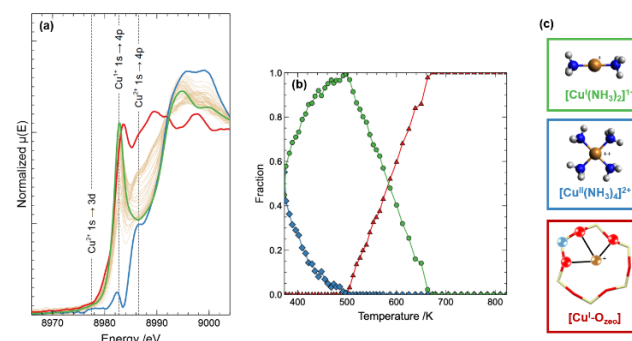
Cu-exchanged small-pore zeolites are currently the catalysts of choice for selective catalytic reduction of nitrogen oxides with ammonia (NH<sub>3</sub>-SCR) due to their hydrothermal stability and high catalytic activity across a wide temperature range. Although the mechanism of NH<sub>3</sub>-SCR and the nature of Cu-active sites has been studied in detail, both experimentally and computationally, the exact nature of these dynamic active sites under reaction conditions is still debated. It is postulated that Cu acts as a redox shuttle and exists in both Cu<sup>I</sup> and Cu<sup>II</sup> oxidation states and in a variety of coordination environments depending on the temperature and the concentration of reactants/products. It has also been reported that hydrothermal ageing of these zeolites (*i.e.*, its prolonged exposure to steam at very high temperatures) results in a decrease of NH<sub>3</sub>-SCR activity especially at higher temperatures. The decrease is associated with change in the electronic and chemical structure of Cu-species. We present here a detailed study elucidating this variation in the state of active sites in Cu-exchanged small-pore zeolites during NH<sub>3</sub>-SCR between 373 K and 823 K, utilizing *operando* X-ray absorption and emission spectroscopy (XAS/XES) complemented with detailed kinetic measurements and supported by density functional theory (DFT) calculations.

## Materials and Methods

CHA and AEI zeolites (Si/Al ~10) were either purchased commercially or synthesized hydrothermally. Cu ion-exchange was performed using aqueous copper acetate solution to achieve appropriate Cu concentration (1-4 wt.-%) in the zeolite. Cu K-edge XAS/XES measurements were performed at the P64/65 beamlines of the German electron synchrotron (DESY). Additional XAS measurements at Al K-edge and Cu L-edge were also performed at the PHOENIX beamline of the Swiss Light Source. For measurements under NH<sub>3</sub>-SCR reaction conditions, the catalysts were loaded into a quartz capillary (1 mm *o.d.*, 20 μm wall thickness, ~5 mm catalyst bed length). The capillaries were heated from below using a hot-air gas-blower and the temperature was varied between 373 K and 823 K. All reactions were carried out at a high GHSV of ~400 000 h<sup>-1</sup> with the following gas composition: 500 ppm NO, 550 ppm NH<sub>3</sub>, 10 vol.-% O<sub>2</sub>, 2 vol.-% H<sub>2</sub>O, and a balance of He. Measured spectra were processed using Athena software package for X-ray absorption near edge structure (XANES) analyses. For extended X-ray absorption fine structure (EXAFS) analyses, spectra were background subtracted, normalized, k<sup>2</sup>-weighted, and Fourier transformed in k-range = 2.7-11 Å<sup>-1</sup>. EXAFS data was fitted using Artemis software package. DFT calculations were performed using the ORCA quantum chemistry package version 4.2. XAS measurements and DFT calculations were further complemented with kinetic measurements and additional characterization including H<sub>2</sub>-TPR, XRD, diffuse reflectance UV-visible spectroscopy, elemental analyses, and IR spectroscopy of adsorbed probe molecules.

## Results and Discussion

XANES and EXAFS were measured on the fresh and hydrothermally-aged Cu-exchanged zeolites under NH<sub>3</sub>-SCR reaction conditions (Figure 1a). Principal component analysis (PCA) was performed on the XANES measured between 373 K and 823 K. PCA identified the presence of three principal components. These components were identified to be (i) mobile Cu<sup>I</sup> species coordinated to NH<sub>3</sub>, *i.e.* [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>1+</sup>, (ii) mobile Cu<sup>II</sup> species coordinated to ammonia, *i.e.*, [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, and (iii) immobile Cu<sup>I</sup> species coordinated to the framework oxygen, denoted as [Cu<sup>I</sup>-O<sub>zeo</sub>] (Figure 1c). The identity of these component was verified experimentally by exposing the catalyst to different gaseous mixtures and computationally with density functional theory calculations. A linear combination fitting (LCF) of the measured XANES spectra was then used to determine the concentration of different Cu species under NH<sub>3</sub>-SCR reaction conditions (Figure 1b). The distribution of Cu species present in the zeolite is described using three different temperature regimes: at low temperatures (<473 K), Cu primarily exists as mobile Cu<sup>I</sup>/Cu<sup>II</sup> species coordinated to NH<sub>3</sub>; at high temperatures (>673 K), Cu primarily exists as Cu<sup>I</sup> species primarily coordinated to the zeolite oxygen and loses its mobility. The mid-temperature regime (between 473 and 673 K), we observe a transition, featuring Cu species that are partially coordinated to adsorbed NH<sub>3</sub> and partially coordinated to the zeolite oxygen. The analogous analysis on hydrothermally aged Cu/AEI sample suggests the presence of a fourth, predominantly Cu<sup>II</sup>, species. This species is postulated to be formed after hydrothermal ageing of the catalysts and is primarily active for NH<sub>3</sub>-oxidation, while not being active for the NH<sub>3</sub>-SCR reaction. This transformation results in the observed catalyst deactivation on hydrothermally aged zeolites.



**Figure 1.** (a) XANES of Cu/AEI under NH<sub>3</sub>-SCR conditions (yellow) and the three principal components identified. (b) Fraction of different Cu-species during NH<sub>3</sub>-SCR determined from LCF. (c) The three principle components identified: [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>1+</sup> (green), [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> (blue), and [Cu<sup>I</sup>-O<sub>zeo</sub>] (red).

## Significance

Selective catalytic reduction of nitrogen oxides with ammonia using Cu-exchanged small-pore zeolites is currently the leading technology to mitigate NO<sub>x</sub> emissions from engine exhaust. A fundamental understanding of the structure of active sites under reaction conditions and after hydrothermal ageing is essential for the development of efficient NH<sub>3</sub>-SCR catalysts.