

Nature of active sites in Cu-exchanged small pore zeolites during selective catalytic reduction of NO_x with NH₃

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Introduction

Cu-exchanged zeolites are the catalysts of choice for selective catalytic reduction of nitrogen oxides (NO_x) with ammonia (NH₃-SCR) due to their high catalytic activity across a wide temperature range (373-823 K). Medium- and large-pore zeolites such as MFI and BEA were explored first but due to extensive formation and agglomeration of extra-framework Al (EFAI) resulting in undesirable CuO_x formation, these catalysts were not stable for long-term operation. The focus of SCR catalyst development therefore shifted to small-pore zeolites such as CHA and more recently AEI and LTA. It is hypothesized that their constrained environment restricts the mobility of EFAI resulting in higher stability. Although the mechanism of NH₃-SCR and the nature of active sites has been studied in detail, both experimentally and computationally, the exact nature of these sites under reaction conditions is still not fully understood. It is postulated that Cu acts as a redox shuttle and exists in both Cu^I and Cu^{II} oxidation states and in a variety of coordination environments depending on the temperature and the concentration of reactants and products.¹ It has also been reported that hydrothermal ageing of these zeolites (*i.e.*, exposure to steam at very high temperatures for several hours) results in a decrease in NH₃-SCR activity especially at high temperatures. The change in the electronic and chemical structure of active Cu-species incurred upon hydrothermal ageing is also not very well understood. Herein we present a detailed study elucidating the nature of active sites in fresh and hydrothermally-aged Cu/AEI catalysts during NH₃-SCR reaction between 373 K and 823 K utilizing *in situ* and *operando* X-ray absorption spectroscopy (XAS) complemented with detailed kinetic measurements and density functional theory (DFT) calculations.

Materials and Methods

AEI zeolites (Si/Al = 5-10) were synthesized hydrothermally following a procedure described by Martin et al.² Cu ion-exchange was performed using aqueous copper acetate solution to achieve the appropriate Cu content (1-4 wt.-%). *Operando* XAS measurements at Cu K-edge 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 performed at the PHOENIX beamline of the Swiss Light Source (SLS). For *operando* XAS measurements under NH₃-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⁻¹ using the following gas composition: 500 ppm NO, 550 ppm NH₃, 10 vol.-% O₂, 2 vol.-% H₂O, and a balance of He. Obtained 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, k²-weighted, and Fourier transformed in k-range = 2.7-12 Å⁻¹. EXAFS data was fitted using Artemis software package. DFT calculations were performed using the ORCA quantum chemistry package version 4.1. XAS measurements and DFT calculations were further complemented with detailed kinetic measurements and additional characterization including H₂-TPR, XRD, DR UV-visible spectroscopy, elemental analysis, FTIR spectroscopy, and X-ray emission spectroscopy.

Results and Discussion

Operando XANES and EXAFS were measured at Cu K-edge on the fresh and hydrothermally-aged Cu/AEI zeolites under NH₃-SCR reaction conditions (Figure 1a). Principal component analysis (PCA) was performed on the XANES spectra measured between 373 K and 823 K. PCA identified the presence of three principal components. These components were identified to be (i) mobile Cu^I species coordinated to NH₃, *i.e.* [Cu^I(NH₃)₂]¹⁺, (ii) mobile Cu^{II} species coordinated to ammonia, *i.e.*, [Cu^{II}(NH₃)₄]²⁺, and (iii) immobile Cu^I species coordinated to the framework oxygen, denoted as [Cu^I-O_{zeo}] (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 in Cu/AEI under NH₃-SCR reaction conditions (Figure 1b). The distribution of Cu species present in the zeolite can be described using three different temperature regimes: at low temperatures (<473 K), Cu primarily exists as mobile Cu^I/Cu^{II} species coordinated to NH₃; at high temperatures (>673 K), Cu primarily exists as Cu^I species primarily coordinated to the zeolite oxygen and loses its mobility. The mid-temperature regime (between 473 and 673 K), we observe a transition from low-temperature to high-temperature regimes and features Cu species that are partially coordinated to adsorbed NH₃ and partially coordinated to the zeolite oxygen. A similar analysis on hydrothermally aged Cu/AEI sample suggested the presence of a fourth predominantly Cu^{II} species. This species is postulated to be formed during hydrothermal ageing and is primarily active for NH₃-oxidation while not being active for the NH₃-SCR reaction.

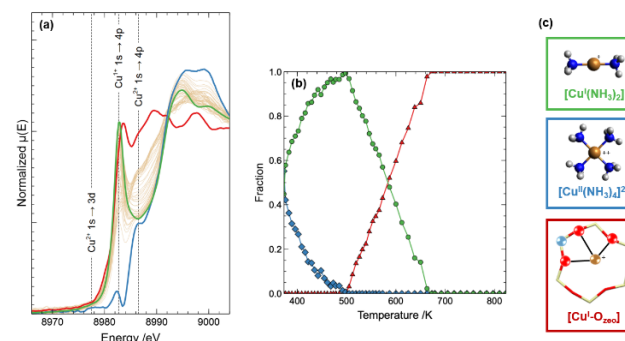


Figure 1. (a) XANES of fresh Cu/AEI under NH₃-SCR conditions between 373 K and 823 K (yellow) and the three principal components identified. (b) Fraction of different Cu species in Cu/AEI during NH₃-SCR determined from LCF. (c) The three principle components identified: [Cu^I(NH₃)₂]¹⁺ (green), [Cu^{II}(NH₃)₄]²⁺ (blue), and [Cu^I-O_{zeo}] (red).

Significance

Selective catalytic reduction of nitrogen oxides with ammonia using Cu-exchanged small-pore zeolites is currently the leading technology to mitigate NO_x 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 NH₃-SCR catalysts.

References

1. J. Am. Chem. Soc. 138, 18, 6028-6048 (2016).
2. Chem. Commun. 51, 11030-11033 (2015).