



Integrated *operando* X-ray absorption and DFT characterization of Cu–SSZ-13 exchange sites during the selective catalytic reduction of NO_x with NH₃

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ABSTRACT

We investigate the Cu oxidation state and coordination environment in copper-exchanged chabazite (Cu–SSZ-13) under *operando* conditions representative of NO_x selective catalytic reduction (SCR) with ammonia, using a combination of X-ray absorption spectroscopy (XAS) experiments, density functional theory (DFT), and first-principles thermodynamics models. Four-fold-coordinated Cu(II) are found to dominate the as-prepared Cu–SSZ-13 and Cu–SSZ-13 under so-called Fast and Slow SCR conditions, in which the NO₂/NO_x ratios are 0.5 and 1, respectively. Under Standard SCR conditions, containing no NO₂ in the feed, mixed Cu(I) and Cu(II) oxidation states are observed along with a reduction in the average Cu coordination. The rate per mole was found to be about equal for Fast and Slow SCR conditions and a factor of two less for Standard conditions. Periodic DFT calculations are used to determine the structure, oxidation state, and relative stability of Cu ions charge compensated with one or two Al and with extralattice oxy, hydroxy, and water ligands. Two-fold Cu(I) and 4-fold Cu(II) species bound with H₂O or OH are found to be most stable over a wide range of conditions. Using the NO₂/NO ratio as a surrogate for the reaction oxidation strength provides good agreement with the observed appearance of Cu(I) species under Standard SCR conditions. The results highlight the role of Cu redox chemistry in SCR catalysis.

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1. Introduction

The control of emissions of nitrogen oxides (NO_x) from on road vehicles is a long-standing fundamental problem in environmental protection. One effective way to remove such pollutants from the exhaust of lean burn engines is by selective catalytic reduction (SCR) using ammonia as a reducing agent [1,2]. Several studies suggest that a Cu-exchanged zeolite is an excellent catalyst to achieve a high SCR activity [1]. With this background, it is surprising that even the nature of the active Cu site is still very much a debated topic, with isolated Cu ions, dimeric Cu species, and bulk-like Cu oxides being proposed as the active sites [3–5]. Recently, the Cu-containing chabazite (CHA), Cu–SSZ-13, has received much attention in this regard due to its robust hydrothermal stability

under SCR conditions [6–8]. The stability of the SSZ-13 zeolite has been attributed to its small-pore size. Indeed, the exchange of Cu into medium-pore sized zeolites (e.g. ZSM-5), seems to destabilize the zeolite structure under SCR conditions [9].

X-ray absorption spectroscopy (XAS) is a powerful technique for catalyst characterization [10–12]. X-ray absorption near edge spectroscopy (XANES) can be used to determine local coordination environments, oxidation states or valence of a given metal atom. Coordinating atoms and interatomic bond distances are measured by extended X-ray absorption fine structure (EXAFS). There are a number of unique ways that have been developed to measure XAS on a catalyst *in situ* in the reaction gas mixture [13]. In many circumstances, simple *in situ* XAS is not sufficient to elucidate the active state of a catalyst, often because the reaction gases bypass the catalyst bed, and the sample does not turn over as it would in a standard benchtop kinetics reactor. Improved spectroscopic measurement techniques, where the catalytic activity is measured while simultaneously characterizing the catalyst, also called *operando*, have been developed for many different applications, including XAS [14–16]. Further improvements upon older XAS cell designs are allowing for ever greater flexibility in operation and more extreme

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operating conditions [17–20]. All of the *operando* XAS data presented in this publication were collected using a cell developed in our lab [20].

Cu-zeolite catalysts have been studied extensively in XAS, especially Cu-ZSM-5 [17,21–25]. The redox nature of Cu makes XANES and EXAFS characterization particularly valuable in understanding the changes in oxidation state and coordination environment as the reaction environment of the catalyst is changed. Recently, Korhonen et al. [5] proposed that the isolated Cu(II) ion was the active site for SCR. These researchers found by XAS and *in situ* ultraviolet and visible (UV-vis) spectroscopy that before and after calcination the Cu remained in the fully oxidized state, but changed coordination from 4 to 3, respectively. On ZSM-5, treated in various environments, both 2 and 3 coordinated Cu have been found, but typically with Cu in the +1 oxidation state [26,27]. As the Cu-CHA system is still rather new, few other studies using XAS have been published. Both Kwak et al. [8] and Fickel et al. [9] have recently studied the activities of the Cu-CHA catalysts. They also found strong hydrothermal stability and very low selectivity towards N₂O. Here, we report *operando* XANES and EXAFS experiments of Cu-SSZ-13 including kinetics for various SCR conditions.

One of the challenges with XANES and EXAFS is to make a connection between the observed spectra and detailed atomic representations of active sites. Density functional theory (DFT) models provide a connection between the X-ray spectroscopies and site structures. Numerous DFT investigations of copper-exchanged zeolites have been reported [28–38] but only a handful have fully taken into account the periodic nature of the zeolite [37–43]. Most of these periodic calculations were done on Cu-free SSZ-13 because its composition is relatively simple [39–43]. These investigations examined the influence of the Si:Al ratio on the chemical reactivity toward hydrogen and ammonia. A purely siliceous (Si:Al=∞) zeolite framework is neutral and chemically inert. Replacing a Si atom (4+) with an Al atom (3+) introduces a negative charge into the framework that is compensated either by cations sitting inside the channels and cages or by protons bonded to framework oxygens and acting as Brønsted acids. One such Al tetrahedral (T-site) provides a potential charge compensation site for Cu(I); two Al T-sites could charge compensate a Cu(II). Recently, such a model was used to interpret an EXAFS analysis of Cu-SSZ-13 in which the coordination of Cu(II) to oxygen was found to be three or four depending on whether the chabazite was calcined or not, respectively [5]. On the other hand, DFT cluster models gave a coordination that was closer to four and did not find any stable configurations when it is reduced to three [44].

The SSZ-13 framework is computationally convenient because of its relatively small supercell size relative to other frameworks of interest, such as Cu-ZSM-5 or even Cu-SAPO-34. To better understand our own EXAFS findings, we examine the local geometry of an exchanged Cu in SSZ-13 in the presence of one and two Al-substituted T-sites (denoted here as “ZCu” and “Z₂Cu”) using a DFT-based periodic supercell model. Because the Cu oxidation state can potentially be influenced both by interactions with the framework and by associated extraframework species, we also compute oxy and hydroxy-type (O_xH_y) adsorbates at an exchanged Cu center, corresponding to the types of surface species expected to be present under wet and oxidizing conditions, and determine their effects on the apparent Cu oxidation state through density of states analysis. We identify a number of Cu(I) and Cu(II) intermediates of differing stoichiometry but similar coordination environments, highlighting the variety of potential structures accessible to an exchanged Cu ion in the SSZ-13 framework. Because they differ in stoichiometry, the relative thermodynamic stability of these various computed Z₂Cu- and ZCuO_xH_y models cannot be determined from their relative energies alone. Here we apply a first-principles

thermodynamics approach [45–50] to compute the relative *free* energies of these sites as a function of the chemical potentials of oxygen and hydrogen. The resultant phase diagrams allow us to identify the most stable Cu(I) and Cu(II) coordination environments and the conditions corresponding to their interconversion. When mapped onto SCR conditions, we find good correspondence between the predicted Cu oxidation states and Cu–O coordination numbers and those inferred from the *operando* X-ray experiments. In particular, we show that the relative NO₂:NO pressure ratio determines the oxidation state of Cu.

The paper is organized as follows. In Sections 2 and 3, we overview our *operando* X-ray absorption spectroscopy experiments and DFT calculations. The XANES and the EXAFS under dry and wet SCR conditions are reported in Section 4.1. Next, the coordination of Cu to the SSZ-13 framework as computed by DFT, as well as the adsorption of O, O₂, OH, O₂H, and H₂O at Cu sites near a single and two Al are described. These DFT results are compiled into an equilibrium phase diagram and compared to our experimental findings in Section 4.2.5. Consequences are discussed in Section 5.

2. Experiment

2.1. SSZ-13 zeolite, catalyst synthesis and characterization

The SSZ-13 zeolite was synthesized via the method recently published by Fickel et al. [7] and is based on the synthesis discovered by Zones et al. [51–54]. 25 g of sodium silicate (Sigma-Aldrich) were added to 20 mL of 1 M NaOH (Sigma-Aldrich) and 32 g of de-ionized (DI) H₂O and mixed for 15 min. 2.5 g of NH₄-Y zeolite (Zeolyst CBV 300) were then added and the mixture was stirred for another 30 min. Finally, 10.5 g of a 25 wt.% aqueous solution containing the structure directing agent, N,N,N-trimethyl-1-adamantylammonium hydroxide (Sachem, Inc.), were added and the solution was mixed for 30 more min. The mixture was split up into four 45 mL Parr PTFE lined acid digestion vessels (Model 4744) and placed in an oven at 413 K for 6 days with agitation at 50 rpm. The resulting product was washed with 1 L of DI H₂O, vacuum filtered, and dried in air overnight. The dried powder was calcined in Air at 823 K for 8 h with a ramp rate of 0.5 K min⁻¹ to produce the Na-form of the zeolite. The H-form was synthesized by mixing the Na-form into a 0.1 M NH₄NO₃ solution for 8 h at 353 K, then the zeolite was dried in air and again calcined at 823 K for 8 h with a ramp rate of 0.5 K min⁻¹.

The resulting SSZ-13 zeolite structure was identified using X-ray diffraction (XRD). The diffraction data are given as [supplementary material](#) and show good agreement with the literature [54–57]. The H-SSZ-13, as synthesized, had a BET surface area of 601 m² g⁻¹ and t-plot pore volume of 0.26 cm³ g⁻¹ [57,58]. Cu was deposited by ion exchange into the H-SSZ-13 zeolite using a Cu(NO₃)₂ salt at a pH=5. Atomic absorption spectroscopy experiments gave a Si:Al ratio of 18:1 and a Cu:Al ratio of 0.11. Further discussion of these methods and their results can be found in the [supplementary material](#).

2.2. X-ray absorption

2.2.1. *Operando* reactor

A custom built downflow *operando* reactor designed for simultaneous X-ray absorption spectroscopy (XAS) and kinetic measurements was used [20]. This technique eliminates issues of bypass, channeling, or diffusion limited reaction, often the pitfalls of *in situ* experiments. The system was adapted to perform experiments for SCR by NH₃ while monitoring the downstream gas concentrations of NO, NO₂, H₂O, CO₂, NH₃ and N₂O by an MKS 2030 FTIR gas analyzer. NO and NO₂ (3000 ppm each in N₂; Matheson Tri-Gas), O₂ (20% in He; Airgas, Inc.), CO₂ (Matheson Tri-Gas)

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