DFT Evidence for Fast NO<sub>x</sub> SCR on Isolated Cu Sites in SSZ-13

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Introduction

Nitrogen Oxides (NO<sub>x</sub>) are pollutants generated in all combustion reactions using air, and are a source of acid rain. The reduction of NO<sub>x</sub> in an oxygen rich environment is a key challenge in meeting more stringent emission regulations. Selective Catalytic Reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> is possible through the usage of zeolite catalysts, such as metal-exchanged SSZ-13. General SCR mechanisms have been proposed, but no detailed microkinetic models are known. In this work, we use DFT simulations to evaluate possible mechanisms for NO<sub>x</sub> reduction by NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub>O over isolated Cu<sup>2+</sup> sites.

Materials and Methods

DFT calculations were performed on a cluster model of Cu exchanged SSZ-13 consisting of six T-sites (Figure 2). Previous periodic super-cell calculations [1] were used as the basis for the structure of the cluster. Calculations were performed using Amsterdam Density Functional (ADF) program using the GGA-PW91 functional for geometry optimization, and B3LYP method for energy calculations.

Results and Discussion

Single Cu<sup>2+</sup> species in the six membered ring of SSZ-13 were proposed as the active sites for SCR [2]. Since SCR happens under oxidative hydrothermal conditions, we first considered the bare copper in this environment and used DFT calculations to generate a free energy diagram of the active site (Figure 1). This diagram was then used to identify likely candidates under SCR conditions that are involved in the catalytic cycle. We used this information, combined with experimental evidence [1], to propose a mechanism, and then evaluated the energy pathway and copper oxidation state using DFT calculations.

Figure 2 shows the resulting energy pathway, we also report the integrated density of states for the Cu atom, which shows the Cu oxidation state cycling between 2+ and 1+. The overall change in energy is favorable towards the reaction, and the proposed active site is thermodynamically favorable. We conclude that isolated Cu<sup>2+</sup> is one possible active site for SCR, and that the mechanism we have proposed reasonably describes this reaction.

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References