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Single center reactivity of Cu(II) sites in copper substituted CHA zeolite followed by *in-situ* electron paramagnetic resonance spectroscopy

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Copper exchanged zeolites are active for the selective catalytic reduction of nitrogen oxides with ammonia.[1] Recently small-pore zeolites and zeotypes with the CHA framework topology has attracted much attention and has been commercialized for use in the abatement of NO_x in diesel exhaust due to favorable properties such as high stability towards hydrothermal ageing and high resistance towards the presence of hydrocarbons. At the same time the simple CHA zeolite structure greatly simplifies the spectroscopic characterization of the materials and allows investigation of one type of site at the time.

Electron paramagnetic resonance spectroscopy (EPR) is very sensitive towards paramagnetic Cu²⁺ and offers the possibility for both quantification and speciation of Cu²⁺ sites with unrivaled sensitivity.[2] Cu⁺ is diamagnetic and does not give an EPR signal.

Recent results obtained on a Cu-CHA zeolite material with Si/Al = 14 and Cu/Al = 0.46 shows that the elucidation of the different copper species is possible using EPR by exposing the Cu-CHA to different gas mixtures.[2]

The time-resolved development of the different Cu²⁺ sites was followed and quantified by EPR in order to follow the oxidation and reduction of the individual sites in the steps of the SCR cycle.[3] In this work Cu-CHA with low concentrations of copper (Cu/Al < 0.1) was exposed to different selective catalytic reduction (SCR) relevant gas mixtures under *in-situ* conditions at high space velocities (400,000 h⁻¹) to resolve the reactivity of each specific copper site. It is shown that during exposure to SCR relevant gas mixtures the different extra-framework Cu species present in Cu-CHA react differently and several examples of this will be presented.

As one example, the rate of oxidation of Cu⁺ to Cu²⁺ is highly dependent of the coordination environment of Cu, and - for at least one of the sites - also on the concentration of NO in the gas phase, see Fig. 1.

The gas flow used in the time resolved experiment in Fig. 1 was switched between

- a mixture of O₂ (10 %), NO (in the interval 250 to 1000 ppm) and balance He, whereupon Cu⁺ is oxidized to Cu²⁺ giving an increase in the signal intensity

and

- NO + NH₃ (1000 and 1200 ppm) and balance He, which resulted in fast and almost complete reduction of Cu²⁺ to Cu⁺ and a decrease in the EPR signal intensity.

The Cu²⁺ species belonging to both site 1 and site 2 can be assigned and quantified on the basis of their EPR spectrum.

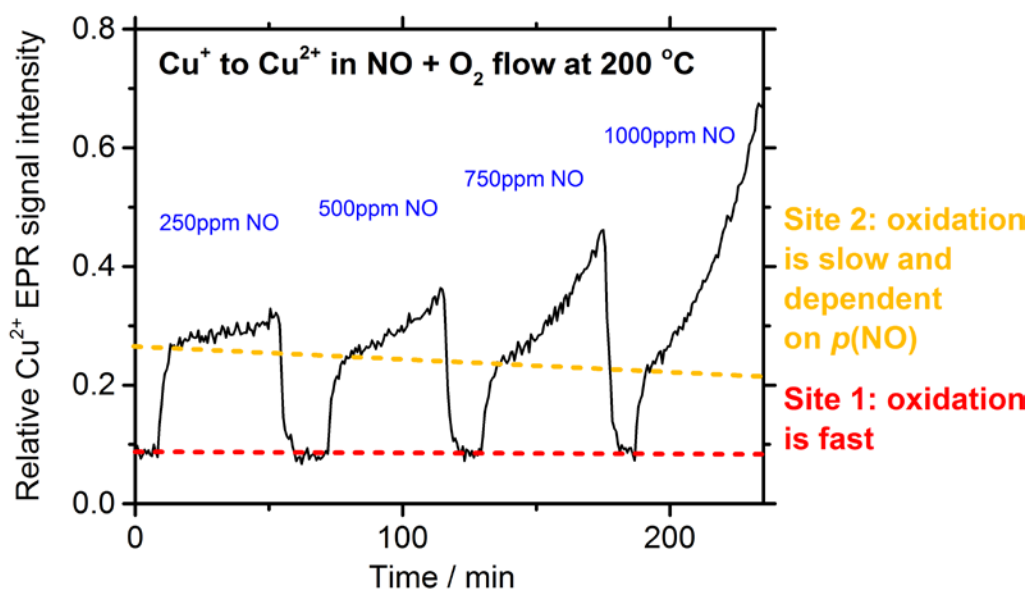


Figure 1. EPR signal intensity followed as a function of time during an in-situ EPR experiment. The intensity is given relative to the signal of all Cu^{2+} in the sample. The sample investigated was fractionated (150-300 μm) Cu-CHA (SSZ-13) with $\text{Si}/\text{Al} = 14$ and $\text{Cu}/\text{Al} = 0.09$. The sample was dehydrated at 250 $^{\circ}\text{C}$ in-situ and reduced in $\text{NO} + \text{NH}_3$ at 200 $^{\circ}\text{C}$ before $t = 0$. The temperature was 200 $^{\circ}\text{C}$ and $\text{GHSV} = 400,000 \text{ h}^{-1}$ throughout the experiment.

Conclusions will be presented for the reaction with SCR relevant gases, NH_3 , NO and O_2 of these materials and the results will be correlated with the recent suggestion for a consistent reaction cycle for the NH_3 -SCR reaction.[3]

[1] U. Deka et. al. *ACS Catal.* **2013**, 3, 413.

[2] A. Godiksen et. al *J. Phys. Chem. C.* **2014**, 118, 23126.

[3] T. V. W. Janssens et. al. *ACS Catal.* **2015**, 5, 2832.