

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

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Abstract Text:

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] 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.[2,3]

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.

It is shown that the rate of oxidation of Cu⁺ to Cu²⁺ is highly dependent of the coordination environment of Cu, and that there is a pronounced difference in the reactivity of the two possible Cu sites in the 6mr of Cu-CHA that can be distinguished based on their distinct EPR signal. Thus the Cu²⁺ species belonging to both EPR active site 1 and site 2 can be assigned and quantified on the basis of their EPR spectrum. The difference in the 6mr Cu sites are suggested to be due to a difference in the position of the two aluminium in the ring, that can be separated by either one or two Si T-sites.

The sample is reduced in NH₃/NO to Cu⁺, flushed with He, and then exposed *in-situ* to either NO/O₂/He or O₂/He at 200°C. For one type of Cu sites in the 6mr, Cu⁺ cannot be oxidized to EPR observable Cu²⁺ in a flow of O₂/He. Additionally, the rate of oxidation in NO/O₂/He depends on the concentration of NO. The other type of 6mr Cu²⁺ site, however, is oxidized fast in both flows. A difference in the reactivity of the two sites can also be observed during reduction in NO/NH₃ and during reduction in H₂.

A discussion of the implications for the activity in the SCR reaction for each of these sites in these materials will be presented and the results will be correlated with the recent suggestion for a consistent reaction cycle for the NH₃-SCR reaction.[4]

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- [3] A. Godiksen et. al. *Top. Catal.* **2016**, Accepted
- [4] T. V. W. Janssens et. al. *ACS Catal.* **2015**, 5, 2832