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Formation and reactivity of nitrates on Cu(II) sites in copper substituted CHA zeolite

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Copper exchanged zeolites are active for the selective catalytic reduction (SCR) of nitrogen oxides with ammonia.[1] The reactivity of small-pore zeolites and zeotypes with the CHA framework topology for removal of NOₓ in diesel exhaust is due to favorable properties such as high stability towards hydrothermal ageing and high resistance towards the presence of hydrocarbons.

One of the key intermediates in the SCR reaction with ammonia is the formation of a nitrate. EPR spectroscopy is very sensitive towards Cu²⁺ and offers the possibility for both quantification and speciation with unrivaled sensitivity.[2] Nitrate coordinated to ion exchanged Cu²⁺ has a distinctive EPR signal, that makes it possible to follow the formation of this species.[3]

Here Cu-CHA with different Si/Al and Cu/Al ratios was first reduced in NO and NH₃ and then exposed to NO and O₂ gas mixtures under in-situ conditions. The formation of [CuNO₃]⁺ was observed on 1Al Cu sites in the CHA structure but not on 2Al Cu sites even though both Cu sites are observed to be oxidized from Cu⁺ to Cu²⁺.

Conclusions for the NH₃-SCR reaction on these materials will be presented.

Figure 1. EPR spectra for Cu-CHA with Si/Al = 15 and Cu/Al = 0.46 during the steps of an in-situ procedure with NH₃ (1200 ppm), NO (1000 ppm) and O₂ (10 %) at 200 °C and GHSV = 400,000 h⁻¹. The difference spectra show that the EPR active nitrate species is first formed in NO + O₂ (step 1 to 3) and then is consumed completely after reaction with NO (step 3 to 4). The nitrate species [CuNO₃]⁺ above the 6mr is shown to the right.