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

Nicklas Møller[1], Oliver Isaksen[1], Anita Godiksen[1], Søren Birk Rasmussen[2], Peter N. R. Vennestrøm[2], Susanne Mossin[1]*

1 – Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Lyngby, Denmark

2 – Haldor Topsøe A/S, Haldor Topsøe alle 1, 2800 Lyngby, Denmark

* slmo@kemi.dtu.dk

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 NO_x 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 Cu^{2+} and offers the possibility for both quantification and speciation with unrivaled sensitivity.[2] Nitrate coordinated to ion exchanged Cu^{2+} 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 NH_3 and then exposed to NO and O_2 gas mixtures under *in-situ* conditions. The formation of $[CuNO_3]^+$ 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 Cu^{2+}.

Conclusions for the NH_3-SCR reaction on these materials will be presented.

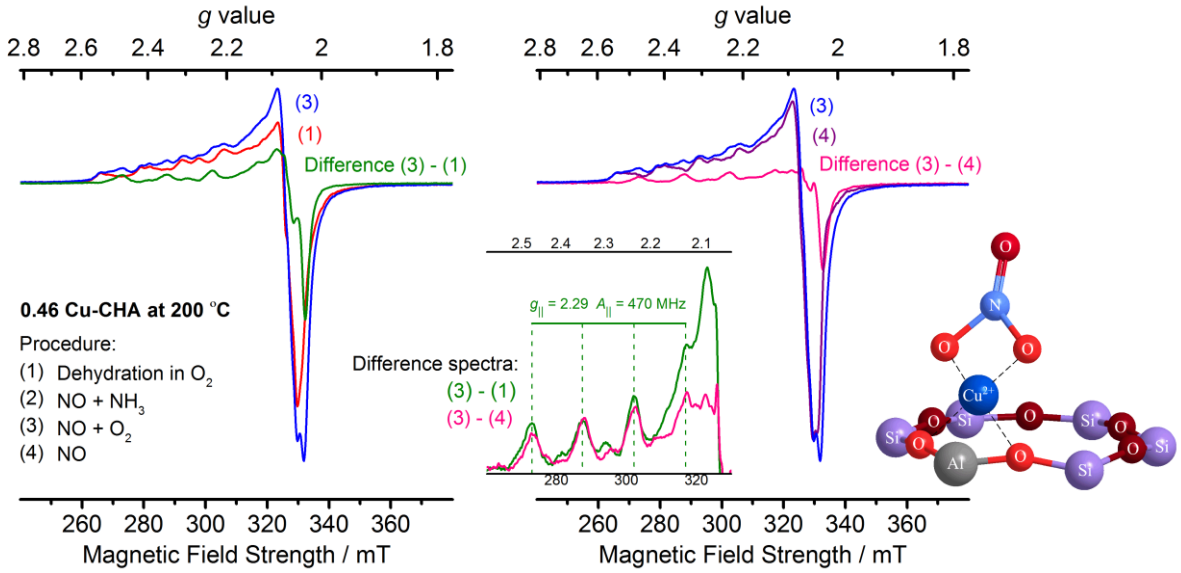

Figure 1. EPR spectra for Cu-CHA with Si/Al = 15 and Cu/Al = 0.46 during the steps of an *in-situ* procedure with NH_3 (1200 ppm), NO (1000 ppm) and O_2 (10 %) at 200 °C and GHSV = 400,000 h^{-1}. The difference spectra show that the EPR active nitrate species is first formed in NO + O_2 (step 1 to 3) and then is consumed completely after reaction with NO (step 3 to 4). The nitrate species $[CuNO_3]^+$ above the 6mr is shown to the right.

[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.