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Site specific reactivity of Cu-CHA with NO, NH₃ and O₂

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Abstract: In-situ electron paramagnetic resonance (EPR) spectroscopy was applied to dilute copper chabazite (CHA) zeolites under gas flows relevant for the selective catalytic reduction of NO with ammonia (NH₃-SCR). Under both reducing and oxidizing conditions, we observed differences in reactivity between the different monomeric copper sites present: When reducing with NO+NH₃, the rate of reduction of Cu⁺ sites depends on NH₃ coverage. The subsequent oxidation with O₂ results in a clean EPR spectrum of only one type of copper site, whereas oxidation in NO+O₂ gives two types of copper sites. The rate of oxidation differs significantly between reaction with O₂ alone and with NO+O₂ together. Thus it was revealed that [Cu(NH₃)₂] complexes, which are regarded to be only weakly associated with the framework, nevertheless have different reactivity depending on the Al distribution in the proximity. The observed differences in reactivity of copper sites has implications for the mechanistic understanding of NH₃-SCR with Cu-zeolites.

Characterization of copper-exchanged zeolites has been carried out with a large variety of spectroscopic methods. The efforts are driven by copper exchanged zeolites being excellent catalysts in the reduction of NOₓ (NO and NO₂) to N₂ via NH₃-SCR, which is one of today’s largest growing applications for zeolite materials. Especially small-pore zeolites, such as CHA, show excellent activity, hydrothermal stability, hydrocarbon tolerance and low production of unwanted N₂O.[1-5] A large selection of experimental methods (IR, XAS, XES, XRD, UV-vis)[6-7] and theoretical approaches (DFT)[8-10] have been applied in recent years for elucidating the properties of Cu-CHA materials. EPR stands out due to the high spectral resolution, fundamentally different selection rules and the applicability under in-situ conditions.[11,12] Recent studies on identical Cu-CHA materials have revealed several well defined Cu sites.[5-7,13,14] This complicates the detailed mapping and kinetic analysis of the SCR reaction on chabazite zeolites where the discussion has mostly focused on the difference between 2AI Cu sites and 1AI Cu sites. It is of vital importance to detailed kinetic studies[13] to be able to distinguish and characterize all sites. Here we present an experimental protocol and a spectroscopic method that is able to reveal significant differences between the different types of 2AI Cu sites present. The reactivity is followed under SCR relevant in-situ conditions and give important insight into the reactivity at single Cu sites.

After dehydration in an O₂ rich atmosphere at temperatures above 200 °C, Cu²⁺ loses coordinated water molecules and binds directly to the zeolite framework. The three most important monomeric sites are, [Cu-OH] close to a 1AI site and two different types of sites with Cu²⁺ in a 6-membered ring (6mr) with 2AI. For a 6mr with two aluminium atoms only para and meta configurations are possible (site A and B, respectively, see Fig. 1) due to Löwenstein’s rule, which states that the Al-O-Al bond motif do not exist in silica-alumina zeolites. The features of the parallel hyperfine quadruplet ([¹⁴⁶⁶Cu both have I = 3/2]) in the EPR spectra are very sensitive to the coordination environment of copper and serve to distinguish site A and B (see Fig.1). Both are 2AI sites which are favored by Cu²⁺ at low copper loadings. On the other hand the 1AI site [CuOH] cannot be detected by EPR at ambient or high temperatures due to fast relaxation.[13,16,17] The energy difference between A and B calculated by DFT is close to the accuracy of the method (22 kJ/mol) with a preference for site A.[10] Recent EPR investigations, however, observe a pronounced preference for the site giving EPR spectrum B in dehydrated Cu-CHA since sufficiently dilute samples gives an EPR spectrum of only B.[16] B has been assigned to the site with a 2AI configuration in meta position. The assignment of the EPR spectrum was based on the known correlation between the charge on the four donor atoms and the parallel spin Hamiltonian parameters and will also be adopted herein.[13]

Figure 1. EPR spectrum (at 200 °C) of Cu-CHA (Cu/Al=0.09) after dehydration (at 250 °C) in 10% O₂ and balance He. The zoom-in shows the parallel region of the spectrum and the assignment of the features.

In this study we have prepared Cu-CHA materials (Si/Al=15) with low Cu content. Assumming random Al distribution, the maximum
Cu loading possible in 2AI 6mr sites is Cu/Al=0.09. Accordingly, one sample with Cu/Al=0.09 was prepared to give the maximum EPR intensity while simultaneously keeping almost all Cu in 2AI sites. A sample with Cu/Al=0.04 was prepared to investigate preferential site B interactions. After dehydration in O₂/He at 200 °C, spin quantification experiments show that 81 % of the copper in the Cu/Al=0.09 sample and ~100 % of the copper in the Cu/Al=0.04 sample are present as EPR active Cu²⁺ species. The amount of EPR silent [CuOH]⁺ is therefore small if it is present at all. EPR confirms the preference for 2AI sites since more than 90% of the observed EPR signal can be assigned to site A and B (Table S1 and Fig. S1). The sensitivity of EPR spectroscopy and the almost exclusive 2AI 6mr site occupation in our samples allow us to investigate the site-specific reactivity differences between site A and B under gas compositions relevant for NH₃-SCR.

In the following, we describe the interaction with gas mixtures relevant to NH₃-SCR studied by EPR.

NO: The EPR spectrum of Cu-CHA exposed to 1000 ppm NO/He at 200°C is identical to the EPR spectrum of the dehydrated Cu-CHA, see Fig. S2. Binding of NO to 2AI Cu²⁺ sites and formation of stable Cu⁺-NO⁺ adducts[20] at this temperature can therefore be ruled out.

NH₃: After application of 1000 ppm NH₃ in He at 100 °C, the EPR active Cu²⁺ sites are quickly transformed from A and B to a single new species, see Fig. 2. Several isosbestic points indicate that any intermediates are too short-lived to be observed. At higher copper dilution the spectral resolution improves since the spin-spin line broadening decreases. The inset in Fig. 2 shows that the spectrum of the copper/amine species found in both samples are identical. They are also very similar to the spectra shown by Blasco et al. obtained at 77 K.[21] The spectrum of the product can be assigned to [Cu(NH₃)₄]²⁺ x = 4 or 5 on the basis of the superhyperfine coupling of the unpaired electron to ¹⁴N from ammonia. See the supporting information and Fig. S3 for a discussion about the assignment. From in-situ X-ray absorption investigations x=4 is found for these samples at similar conditions[21] and we therefore conclude that the dominant species is [Cu(NH₃)₄]²⁺. Reduction of [Cu(NH₃)₄]²⁺ does not take place at 100 °C in a flow of 1000 ppm NH₃, see Fig. S3. Upon heating from 100 to 150°C the intensity of the EPR signal (calculated as the double integral) starts to decrease slowly, indicating an increase in the rate of reduction, which further increases upon heating to 200 °C.

NO+NH₃: Reduction with both NO and NH₃ together at 200 °C or above is very fast.[17] In order to follow the reaction in real time the temperature was decreased to 100 °C and the sample was exposed first to NO and then to NO+NH₃ (each 1000 ppm). When ammonia reaches the sample, the EPR signal intensity drops fast and the EPR spectrum of [Cu(NH₃)₄]²⁺ appears. Once the establishment of the ammine species is complete the reduction continues, but at a slower rate than the initial reduction rate, see Fig. 3. Based on this observation we argue that the reduction of Cu²⁺ in NO+NH₃ at 100 °C is slightly inhibited by excess NH₃ since [Cu(NH₃)₄]²⁺ reacts slower than less saturated species.

Figure 2. In-situ EPR spectra of the reaction of dehydrated Cu/Al=0.09 with 1000 ppm NH₃ at 100 °C. Thin lines are intermediate spectra spaced by 45 sec. The parallel features of all three EPR observable sites are indicated. Inset: The 2nd derivative EPR spectrum in the perpendicular region is included to enhance the super hyperfine pattern. The data for the Cu=0.04 sample at the same conditions is given for comparison.

Figure 3. First derivative in-situ EPR spectra of the reaction of Cu²⁺ in 6mr sites on the Cu/Al=0.09 sample with 1000 ppm NO+NH₃ at 100 °C. Grey lines are intermediate spectra spaced by 45 sec after t = 0. Inset: Development in the relative doubly integrated EPR spectrum reduction. The spectra shown are indicated with larger dots. Slopes are given as a guide to the eye. (For reduction in NO+NH₃ at 200 °C, see Fig. 4).

1st NO+NH₃, 2nd O₂: After full reduction in NO+NH₃ at 200 °C (and subsequent He flush to remove weakly adsorbed NO and NH₃) the samples were exposed to 10 % O₂. After reduction in NH₃+NO the dominant Cu species is expected to be linear [Cu(NH₃)₂]+ without any strong coordination to specific zeolite framework environments.[22] When the oxidant is O₂ the [Cu(NH₃)₂]+ complex shows a preference towards oxidation into site A, see top-part of Fig. 4. Site A appears exclusively and is isolated for the first time. The EPR spectrum can be described by the spin Hamiltonian parameters g⊥=2.063 and g∥=2.328, see Table S3 and Fig. S5. This observation reveals that despite the loose coordination to the
zeolite framework and the mobility of [Cu(NH$_3$)$_2$]$^{2+}$ described in several publications,[23,24] the reactivity of this complex towards oxidation depends on the Al-distribution in the zeolite microenvironment.

1$^{st}$ NO+NH$_3$, 2$^{nd}$ NO+O$_2$: After full reduction in NO+NH$_3$ (same as above) the sample was exposed to 10% O$_2$ and 1000 ppm NO. The oxidation in NO+O$_2$ is faster than in O$_2$ alone. Site A appears again, but in this case site B also appears. For the sample with Cu/Al=0.09 the experiment was performed for concentrations of NO from 250 ppm to 1000 ppm, see Fig. 4, bottom. In all cases site A appears almost instantaneously (green arrows in Fig. 4 and Fig. S5). The rate of formation of site B depends on the NO partial pressure with the initial rate being first order in p(NO). [CuNO$_3$]$^{2-}$ has a distinct EPR spectrum which was not observed at elevated temperatures after oxidation with NO+O$_2$ on the samples investigated here, see Fig. S2. This provides further evidence that temperature-stable [CuNO$_3$]$^{2-}$ species are formed in samples containing [CuOH]$^+$ but not for site A or B.[$7,10,14$] Formation of transient [CuNO$_3$]$^{2-}$ is not excluded on site A and B, however. This is discussed in more detail below.

![EPR spectra diagram](image)

**Figure 4.** Top: In-situ EPR spectra of Cu-CHA (Cu/Al=0.04) after exposure to NO+NH$_3$ and oxidation with either NO+O$_2$ (orange) or O$_2$ alone (green). Inset: Time-resolved EPR signal intensity during the in-situ measurement. The plotted spectra are marked with dots. Bottom: Time-resolved EPR signal intensity during in-situ measurement of Cu-QHA (Cu/Al=0.09). Intervals with NO+NH$_3$ alternate with intervals with O$_2$+NO at different NO partial pressures. Flushing of the sample with He (5 min) was performed just before the marked changes of flow. Green arrows indicate spectra which are recognized to be almost exclusively A. During reduction p(NO)=p(NH$_3$)=1000 ppm, p(O$_2$)=10 % when in use.

**Discussion**

Site A and B react equally fast with NH$_3$ forming the EPR active [Cu(NH$_3$)$_2$]$^{2+}$. The complex is stable in NH$_3$ flow at 100 °C, but is reduced slowly at higher temperatures. The reduction is much faster at all temperatures when both NO and NH$_3$ are present. In accordance with XAS investigations, we suggest that [Cu(NH$_3$)$_2$]$^{2+}$ is formed after reduction in NH$_3$ or in NO+NH$_3$.[6,22] For 2Al sites a second cation, NH$_4^+$ (or H$^+$), is required for charge-balance. Due to Coulomb repulsion, the second cation may prefer to be on another face of the Al-T-site and thus in another cage of the CHA structure. In this way the reaction pathway of reoxidation of [Cu(NH$_3$)$_2$]$^{2+}$ to A and B can potentially be different. We observe experimentally under flow conditions at 200 °C that [Cu(NH$_3$)$_2$]$^{2+}$ → Site A is at least an order of magnitude faster than [Cu(NH$_3$)$_2$]$^{2+}$ → Site B when the oxidant is O$_2$. The difference in reactivity of the sites is also observed by oxidation with NO+O$_2$ since the formation of A is too fast to follow with the current time resolution, whereas the formation of B can be followed easily. The rate of formation of B is found to be of first order in p(NO) when oxidizing with NO+O$_2$.

[CuNO$_3$]$^{2-}$ was not observed experimentally; nevertheless we suggest that Cu$^+$ reacts with NO and O$_2$ to form [CuNO$_3$]$^{2-}$.[7,25] but that this is unstable in the 2Al 6mr site.[14] The [CuNO$_3$]$^{2-}$ intermediate and the second cation is suggested to proceed to generate a Cu$^{2+}$ site (A or B) and products with the sum formula NH$_3$NO$_3$ (or HNO$_3$). This is the sum formula for ammonium nitrate and nitric acid but neither of these species are expected to survive at 200 °C and they will likely decompose immediately even if formed transiently.

**Conclusion**

In summary, we have shown how in-situ EPR can be used to follow the individual Cu sites present in Cu-CHA at temperatures and gas mixtures relevant for the NH$_3$-SCR reaction. Selecting dilute Cu-CHA samples provided two advantages: Fewer different Cu species are present and the dilution of paramagnetic species improved the resolution of the EPR spectra allowing the assessment of super hyperfine patterns. The reaction of Cu species with gas phase molecules was slowed down by lowering the temperature or the NO concentration. For the first time, it was observed experimentally how the reactivity differs significantly between copper ions associated with different 2Al sites in the CHA structure. Site A is more reactive towards oxidation in SCR relevant mixtures than site B. Since the oxidation of Cu$^+$ is suggested to be the rate-determining step this implies a higher activity of site A towards SCR at 200 °C.

**Experimental section**

Samples were prepared with by ion exchange of CHA zeolites with Cu(CH$_3$COO)$_2$ in the same way as described in [$8$]. EPR measurements were performed with a Bruker EMX X-band spectrometer using the setup described in [$13$]. Briefly described, approximately 20 mg of sample was immobilized with quartz wool in tubes with an inner diameter of 4 mm and exposed to a gas flow of 200 mL/min corresponding to GHSV = 400,000 h$^{-1}$. Each individual EPR spectrum was obtained over approximately 35 seconds and the field was swept for additional 10 seconds giving a time resolution of 45 s in the time resolved plots shown in this work. The EPR parameters were: Frequency 9.45 GHz, modulation 100 kHz, modulation amplitude 8 G and field sweep 220 to 400 mT.
For all investigations, the samples are initially dehydrated in flow of 200 mL/min O₂/He during temperature ramp at 7 K/min to 250°C, and kept at this temperature for at least 1 h whereupon all copper ions are fully oxidized.[8] Afterwards the sample is cooled to the desired temperature at 7 K/min and the new gas mixture is admitted at 200 mL/min.

The data treatment followed the same procedure as in [13,14]. Simulation of EPR spectra was carried out using Easyspin[26] with a careful fitting of g and A-strain to account for the angular anomaly seen in the perpendicular region of the experimental spectra.[27–29] EPR intensities, I, for spin quantification purposes are obtained by double integration of background-corrected EPR spectra. The intensities are given relative to the start spectrum (always recorded at room temperature) and are corrected for the measurement temperature, see Eq. (1):

\[ I(T) = \frac{I(T_{start})}{I(293 \text{ K})} \times \frac{T}{293 \text{ K}} \]  

(1)

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Keywords: Copper • EPR spectroscopy • in-situ spectroscopy • SCR • site-specific reactivity

Using in-situ EPR spectroscopy it is possible for the first time to differentiate between the two Cu sites in the 6 membered ring in Cu exchanged chabazite zeolites. The composition of the oxidizing gas flow determines whether a single Cu site or both Cu sites are oxidized.