



<b>Structure determination of well defined Cu(I) adducts, <i>in situ</i> synthesized, in Cu(I)-zeolites cavities: a combined EXAFS/XANES study in the multiple scattering approach</b>		<b>Experiment number:</b> <b>CH-1015</b>
<b>Beamlne:</b> BM8 GILDA	<b>Date of experiment:</b> from: 28/11/2001 to: 03/12/2001	<b>Date of report:</b> 29/08/2003
<b>Shifts: 15</b>	<b>Local contact(s):</b> Francesco D'Acapito	<i>Received at ESRF:</i>
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We report an high resolution XANES study able to determine both oxidation state and of local symmetry of Cu species hosted in Zeolite in interaction with NO, i.e. the key problem in understanding the ability of Cu-zeolites to convert NO into O<sub>2</sub> and N<sub>2</sub>. XAFS measurements, were performed in transmission mode at GILDA BM8 beamline using a cell allowing *in situ* sample activation up to 800 K, cooling down to 80 K and gas dosage [1]. The figure reports the 80 K XANES spectra of Cu<sup>+</sup>-ZSM-5 zeolite under vacuum (solid line) and after interaction with NO (dashed line), and after increasing the temperature up to 300 K (dotted line). For comparison, the spectra of a Cu<sup>2+</sup>-ZSM-5 sample, is shown (scattered spectrum). The part b of the figure reports the corresponding derivatives. Main features of XANES and derivative spectra are reported in the Table. The spectrum recorded *in vacuo* (full line), is characterized by a very intense 1s→4p pre-edge peak at 8983.5 eV accompanied by a less intense but still well resolved component at 8986.6 eV (observed under the high resolution configuration adopted in this work). This has allowed to ascribe the 1s→4p<sub>xy</sub> transition at the more intense peak at 8983.5 eV, and the 1s→4p<sub>z</sub> transition, at the less intense component.

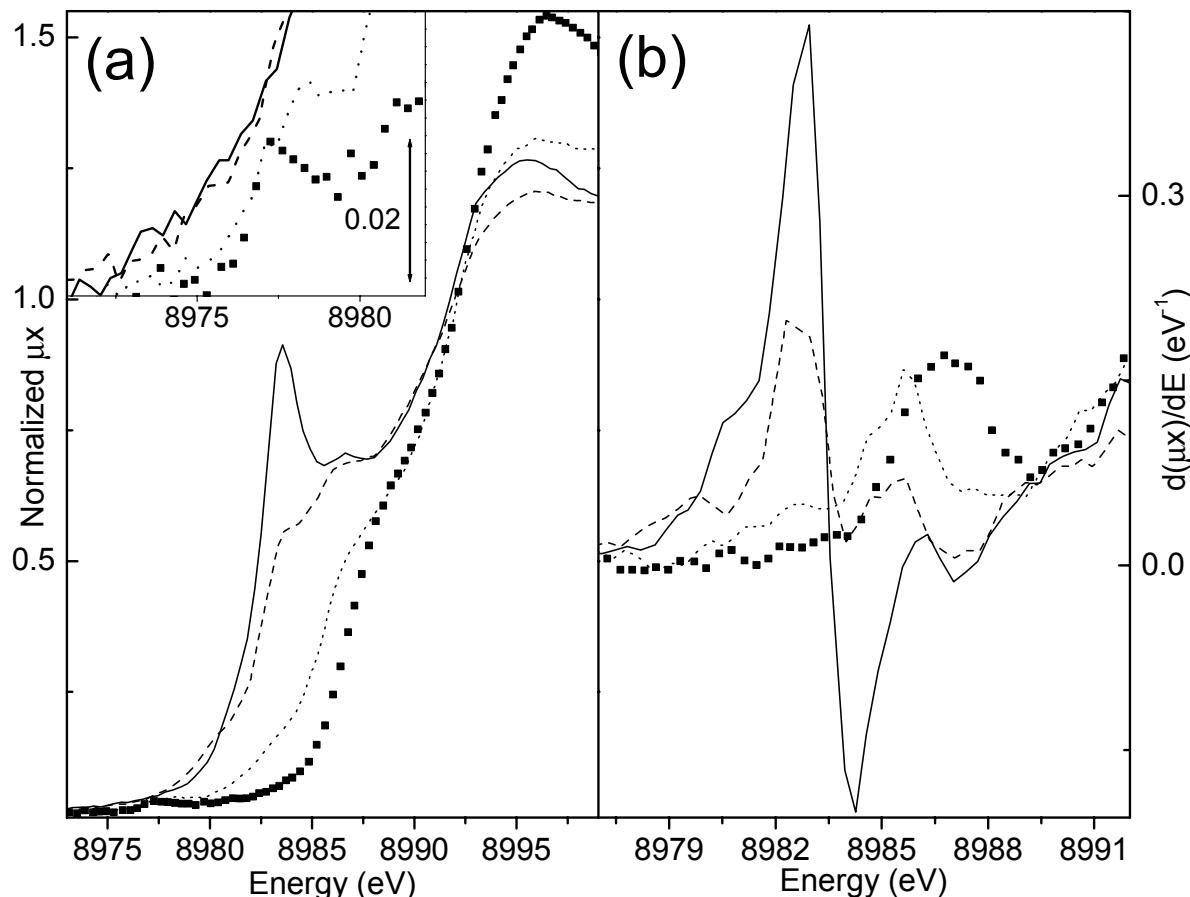
Upon dosing NO, at 80 K (dashed line), Cu<sup>+</sup>(NO)<sub>2</sub> complexes are formed and the XANES region becomes more structured, with the appearance of a new component at lower energy ( $\approx$  8979.9 eV), being the intense peak around 8983 eV slightly shifted and strongly reduced. These facts are interpreted in terms of the splitting of the p<sub>xy</sub> orbital into p<sub>x</sub> and p<sub>y</sub>. The p<sub>x</sub>/p<sub>y</sub> and p<sub>y</sub>/p<sub>z</sub> splitting is of 3.8 and 2.6 eV respectively.

Upon increasing the temperature in NO atmosphere (dotted line spectrum) a significant blue shift of both edge and pre-edge features is observed, indicating that a consistent fraction of the cuprous ions has been oxidized to the cupric state. By using the XANES spectrum of the Cu<sup>2+</sup>-ZSM-5 sample activated at room temperature (scattered spectrum) as a model of ZSM-5 with 100% cupric ions, we estimate that NO has been able to oxidize 80 % of the overall copper. Note that the presence of majority fraction of cupric species is also testified by the appearance of the very weak, dipole forbidden, 1s→3d transition (inset). Also in this case we

are dealing with a complete rupture of the degeneration of the 4p level, being both  $1s \rightarrow 4p_x$  and  $1s \rightarrow 4p_y$  transitions upward shifted by approximately 3.0 eV as a oxidation of cuprous species. The higher energy  $1s \rightarrow 4p_z$  transitions can not be safely identified being now around 8989-8990 eV, *i.e.* in the edge of the X-ray absorption spectrum. This study has been published in ref. [2] for the Cu-ZSM-5 zeolite. A more complex study on the Cu-Mordenite system, not discussed in this report for the sake of brevity has been published in ref. [3]. An overview on the methodology adopted by our group during in situ XANES experiments is reported in ref. [4].

Table: (Zeo = ZSM-5 zeolite; sh = shoulder; I= intensity; Deg = Degenerate).

Sample	$1s \rightarrow 4p_x$ Position (eV)	I	$1s \rightarrow 4p_y$ Position (eV)	I	$1s \rightarrow 4p_z$ Position (eV)	I	$1s \rightarrow 3d$ Position (eV)	I
Cu <sup>+</sup> -Zeo	Deg. with $1s \rightarrow 4p_y$		8983.5	0.92	8986.6	0.71	-	-
+NO 80K	8979.9 sh	0.15	8983.7 sh	0.56	8986.3 sh	0.68	-	-
+NO RT	8982.9 sh	0.15	8987.0 sh	0.53	in the edge		8978.3	0.05
Cu <sup>2+</sup> -Zeo	Deg. with $1s \rightarrow 4p_y$		8988.0 sh	0.56	in the edge		8977.8	0.04



- [1] C. Lamberti et al., presented at EMRS 2002; *Nuclear Instr. Meth. B*, **200** (2003) 196-201.
- [2] C. Prestipino, G. Berlier, C. Lamberti et al. *Chem. Phys. Lett.*, **363** (2002) 389-396.
- [3] F. X. Llabrés i Xamena, C. Lamberti et al., *J. Phys. Chem. B*, **107** (2003) 7036-7044.
- [4] C. Lamberti, S. Bordiga, C. Prestipino, et al. *Phys. Chem. Chem. Phys.*, **5** (2003) in press.