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XAFS Study of $\text{Cu}^{\text{I}}\text{-Y}$ and $\text{Cu}^{\text{II}}\text{-Y}$ Interacting with CO and NO

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Abstract We report a study of the local copper environment in $\text{Cu}^{\text{I}}\text{-Y}$ prepared by gas phase reaction of H-Y with CuCl and in $\text{Cu}^{\text{II}}\text{-Y}$ prepared by conventional ion exchange with aqueous cupric salt. For the $\text{Cu}^{\text{I}}\text{-Y}$ sample, the effect of the interaction with CO and NO will also be reported. XANES, UV-Vis and IR (NO dosed at 77 K) techniques prove that the copper species in the prepared samples have the desired oxidation state. Reduction of $\text{Cu}^{\text{I}}\text{-Y}$ with CO leads to the formation of small copper clusters well identified by EXAFS, XANES and UV-Vis spectroscopies, while interaction with NO partially oxydate Cu^{I} to Cu^{II} . For both as prepared $\text{Cu}^{\text{I}}\text{-Y}$ and $\text{Cu}^{\text{II}}\text{-Y}$ samples EXAFS does not observe first shell Cu-Cu bond lengths, so excluding the presence of "so called" Cu-dimers in zeolites prepared following our methods.

1. RESULTS AND DISCUSSION

Copper exchanged zeolites (ZSM-5 and Mordenite) have recently reached a great interest in the direct conversion of NO into N_2 and O_2 [1,2], so stimulating the investigation of other copper exchanged zeolites. While $\text{Cu}^{\text{II}}\text{-Y}$ was prepared by conventional ion exchange with aqueous cupric salt, $\text{Cu}^{\text{I}}\text{-Y}$ was prepared by an original gas phase reaction of H-Y with CuCl already detailed elsewhere [3,4]. XAFS measurements, were performed at 300 K in transmission mode at GILDA D8 GRG beamline [5] of ESRF in Grenoble F, (proposal CH132), equipped with a double crystal Si(331) monochromator detuned at 1/3 of the rocking curve to avoid harmonics and operating in a dynamical sagittal focusing mode [6]. Incident and transmitted beams were recorded with a 1.0 Atm N_2 filled (10 % efficiency) and with a 0.3 Atm Ar filled (80 % efficiency) ionization chamber respectively. A sampling step of 0.2 eV for the XANES part of the spectra and a variable sampling step, giving rise to $\Delta k_{\text{max}} = 0.05 \text{ \AA}^{-1}$ for the EXAFS part and an integration time of 3 s/point have been adopted. The energy resolution in the experimental condition was estimated to be 0.5 eV at Cu-K edge. A Cu metal foil has been used for the angle/energy calibration. XAFS experiments have been performed using an *ad hoc* cell already described elsewhere [8], allowing *in situ* sample activation up to 800 K and gas dosage to be made. For each sample the EXAFS spectrum was acquired three times under the same experimental conditions and extracted $\chi(k)$ (using four cubic splines to compute the atomic adsorption) have been averaged before the EXAFS data analysis, which has been performed following standard procedures [8] using Michalovicz programs [9]. The $\text{Cu}^{\text{I}}\text{-Y}$ sample has been measured at RT in the following conditions: i) vacuum; ii) after interaction with CO; iii) after interaction with NO; iv) after reduction at 500 K in CO atmosphere for one hour and subsequent evacuation (hereafter indicated as samples *Y*, *YCO*, *YNO* and *Yrid* respectively). The $\text{Cu}^{\text{II}}\text{-Y}$ sample has been measured at RT only in vacuum conditions (hereafter indicated as sample *Y2*). For this samples the activation treatment has been performed only at 400 K to avoid the thermal autoreduction of Cu^{II} species. Fig. 1 reports the normalized XANES spectra of all samples, together with those of Copper metal, Cu_2O and CuO model compounds. *Y*, *YNO* and *Yrid* samples show a XANES profile very similar to that of Cu_2O , denoting that the main copper species present in these sample exhibit the oxidation state I. However, the pre-edge lineshape of *Yrid* is characterized by an adsorption at lower energy, typical of copper in the metallic state. Spectrum of sample *YCO*, shows and edge at the same energy of Cu_2O , but the intensity of its $1s \rightarrow 4p$ dipole-allowed transition at 8983 eV is strongly damped. *Y2* sample has a XANES spectrum typical of Cu^{II} species; even if scarcely visible in Fig.1, both *Y2* and CuO samples exhibit the same weak adsorption at 8977 eV due to the dipole-forbidden $1s \rightarrow 3d$ transition. k^2 -weighted Fourier transform (FT), calculated in the range $3\text{-}13 \text{ \AA}^{-1}$ using a Kaiser window with $\tau = 2.5$ of all zeolitic samples are reported in Fig. 2; for comparison the FT of Cu_2O and copper metal (measured at 77 K and k^2 transformed in the range $3\text{-}20 \text{ \AA}^{-1}$) are also present. No phase correction has been performed in the spectra reported in Fig. 2. Concerning samples measured in vacuum, both *Y2* and *Y* exhibit a first coordination shell typical of Cu-O distances and no signal of Cu-Cu are observed. The higher intensity of the first shell Cu-O peak in *Y2*, with respect to *Y*, is related to the higher first shell coordination number of Cu^{II} . The $d(\mu\text{x})/dE$ spectra of samples *Y2*, *Y* match very close with those of CuO and Cu_2O model compounds (see Fig. 3). XAFS results thus prove that we were able to prepare isolated Cu sites in Y zeolite, having the desired oxidation state. *Yrid* sample, shows both Cu-O and Cu-Cu first shell coordination distances. This means that it contains both Cu^{I} isolated species and small metal clusters trapped in the faujasitic supercage (11 Å in diameter). The presence of an higher shells signal typical of second, third and fourth coordination shells of FCC structures clearly show that we are dealing with metal cluster having a size comparable to those of the supercage. Powder XRD measurement on *Yrid* sample does not reveal the presence of Cu metal, implying that the size of the cluster must be smaller than 40 Å in diameter. The hypothesis that CO reduction give rise to Cu cluster trapped in the zeolite cages is thus very plausible. *Yrid* sample still contains an high number of isolated Cu^{I} species since its μx and $d(\mu\text{x})/dE$ spectra are still more close to that of Cu_2O . The strong Cu-Cu signal in the FT is mostly due to the higher backscattering power of Cu (compared to O). Quantitative results of our EXAFS analysis will be reported at the conference and discussed with the literature data [11,12]. Our results will be

strongly supported by UV-Vis and IR study of dosed CO and NO molecules. We thank the ESRF Chem. Lab.

Figure 1: XANES spectra: dashed, full and dotted curves indicates samples where Cu species have mainly 0, I and II as oxidation state.

Figure 2: k^3 weighted FT performed in the 3-20 $\text{\AA}^{-1}$ (Cu metal foil) and 3-13 $\text{\AA}^{-1}$ (other samples) range.

Figure 3: $d(\mu x)/dE$ spectra of Y2, Y and Yrid samples (parts a, b and c respectively) compared with spectra of model compounds.

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