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C. Lamberti, M. Salvalaggio, S. Bordiga, F. Geobaldo, G. Spoto, et al.. CuI Sites in CuI–ZSM–5 : A XAFS, IR and Computer Graphics Study. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-905-C2-906. 10.1051/jp4:1997274 . jpa-00255357

HAL Id: jpa-00255357

<https://hal.science/jpa-00255357>

Submitted on 1 Jan 1997

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Cu^I Sites in Cu^I-ZSM-5: A XAFS, IR and Computer Graphics Study

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Abstract IR and XAFS have been employed to investigate the local environment of Cu^I in Cu^I-ZSM-5 prepared by gas phase reaction of H-ZSM-5 with CuCl. Both XAFS and IR measurements show that copper species are monodispersed Cu^I ions, occupying highly unsaturated sites easily accessible to small ligand molecules. Cu^I-ZSM-5 prepared in this way represent a model solid for investigating the structure of isolated Cu^I sites in zeolites. EXAFS analysis reveal that, in vacuum conditions, Cu^I cations are surrounded by 2.5 ± 0.3 oxygens at 2.00 ± 0.02 Å. The combined use of EXAFS, IR and computer graphic simulations allows to infer that Cu^I ions in Cu^I-ZSM-5 are located in two families of sites.

1. RESULTS AND DISCUSSION

Copper exchanged zeolites (ZSM-5 and Mordenite) have recently reached a great interest in the direct conversion of NO into N₂ and O₂ [1,2]. The most active samples are more than 100% exchanged (where, a 100% exchange is defined to occur when a Cu²⁺ ion is introduced for two Al framework atoms) [1]. The characterization of these samples, and thus the correct understanding of the NO conversion mechanism is very complex because of the co-presence of copper species in different oxidation and coordination states, see e.g. ref. [3]. We have prepared a Cu^I-ZSM-5 sample following a gas phase reaction with CuCl as already detailed elsewhere [4-6]. The total erosion of the 3611 cm⁻¹ IR band due to the ν(OH) of internal bridged Si-(OH)-Al groups in the exchanged samples, indicates that all the protons have been substituted by a Cu⁺ counterion, so yielding a 200% exchange. For IR measurements, thin self-supporting wafers of each zeolite were prepared and activated under dynamical vacuum at 673 K for 2 hours, inside an IR cell, designed to allow *in situ* high-temperature treatments, gas dosage and low-temperature measurements to be made. The IR spectra were recorded, at 2 cm⁻¹ resolution, on a BRUKER FTIR66 spectrometer equipped with an MCT cryo-detector. It has been shown that CO forms at RT Cu^I(CO)_n (n=1,2) adducts at RT, characterized by bands at 2157 cm⁻¹ (monocarbonyl) and 2178 and 2151 cm⁻¹ (symmetric and asymmetric modes of the cis-dicarbonyl) [5,7]. The capacity of Cu^I to coordinate ligands to complete its coordination sphere is not exhausted with the formation of Cu(CO)₂ species. This fact is clearly visible in Fig. 1, where the adsorption of CO at ~110 K is studied as a function of the CO equilibrium pressure: the formation of Cu(CO)₃ complexes by addition of CO to the pre-existing Cu(CO)₂ dicarbonyls is well evident, as demonstrated by the new bands at 2192 and 2167 cm⁻¹ and by the parallel decrement of the 2178 cm⁻¹ dicarbonyls component. The 2164 cm⁻¹ band appears to be constituted by a doublet: this means that we are, most probably, dealing with two family of very similar tricarbonyls species formed on slightly different families of Cu^I sites. An important observation must be made: while at both RT and at ~110 K the Cu^I(CO) → Cu^I(CO)₂ transformation is total [5,7], the same does not occur at ~110 K for the Cu^I(CO)₂ → Cu^I(CO)₃ transformation, see Fig. 1. In fact the 2178 and at 2151 cm⁻¹ bands are not completely eroded upon increasing the CO equilibrium pressure. This fact cannot be ascribed to an insufficient amount of dosed molecules, because an increase of the equilibrium pressure, at ~110 K, does not appreciably modify the situation. This confirms that we are probably dealing with two different families of Cu^I sites differing on the fact that, at ~110 K, only one is able to coordinate three CO molecules. Moreover, a computer graphic study shows the presence of two family of sites where Cu^I is two-fold and three-fold coordinated with framework oxygens [7]. XAFS measurements, were performed at 300 K in transmission mode at EXAFS1 station of LURE, Orsay (proposal CK007), equipped with a Si(331) channel-cut monochromator and with air filled ionization chambers using a sampling step of 0.5 and 2 eV for the XANES and EXAFS spectra respectively. A Cu metal foil has been used for the angle/energy calibration. Data have been collected on the dehydrated sample using an *ad hoc* cell already described elsewhere [8]. The presence of a sharp peak at 8982 eV, in the XANES spectrum of Cu^I-ZSM-5 outgassed *in vacuo*, is unambiguous proof that we are dealing with Cu^I ions (see Fig. 2). The EXAFS spectrum was acquired three times under the same experimental conditions and extracted χ(k) (using B⁵ polynomial function to compute the atomic adsorption) have been averaged before the EXAFS data analysis, see Fig 3a. Standard deviation calculated from the averaged spectra was used as an estimate of the statistical noise for the evaluation of the error associated with each structural parameters applying the test proposed by Joyner *et al.* [9]. The absence of any beats in the oscillations of χ(k) suggests that the main contribution to the overall χ(k) signal is due to only one coordination shell. The EXAFS data analysis has been performed following standard procedures [10] using Michalovicz programs [11]. k³-weighted Fourier transform (FT), calculated in the range 3-13 Å⁻¹ using a Kaiser window with τ = 2.5 (see Fig. 3b), shows only one prominent peak located at ca. 1.5 Å without any correction for the phase shift. No contribution in the typical range of Cu-Cu bond distance was observed. This result clearly confirms the absence of copper clusters in the sample. Data analysis performed in the frame of single scattering curved wave approximation extracting the experimental phase shift and amplitude functions from Cu₂O model compound results in a first Cu^I coordination shell formed by 2.5 ± 0.3

oxygen atoms at $2.00 \pm 0.02 \text{ \AA}$ and characterized by $\sigma = 7.3 \cdot 10^{-2} \pm 10^{-2} \text{ \AA}$ (being for, Cu_2O , $\sigma = 6.8 \cdot 10^{-2} \pm 10^{-2} \text{ \AA}$). EXAFS results are thus indicative of the low-coordination number and the high coordinative unsaturation of Cu^{I} ions, in agreement with the IR data. The quality of the fit can be evaluated from Fig. 3c and by the symmetry of the imaginary part with respect to the modulus of the phase corrected FT reported in Fig. 3d [12]. The important assistance of F. Villain is acknowledged.

Figure 1: IR spectra of CO dosed at $\approx 110 \text{ K}$: equilibrium pressures from 0.1 to 10 Torr.

Figure 2: Near edge spectra of (from top to bottom): Cu-ZSM-5, Cu_2O and CuCl_2 .

Figure 3: a) Experimental $k\chi(k)$; b) k^3 weighted FT in the range 3-13 $\text{\AA}^{-1}$ without phase correction; c) corresponding back-FIT in the 1.0-2.2 $\text{\AA}$ (dashed line) and best fit (full line); d) modulus and imaginary part of the phase corrected k^3 weighted FT of $\chi(k)$ in the range 3-13 $\text{\AA}^{-1}$.

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