



Experiment title: Modification of the Cu ^I sites environment in Cu ^I -zeolites under the effect of interaction with NO and CO dosed at different equilibrium pressures	Experiment number: CH-542
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Local contact(s): Francesco D'ACAPITO	Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

C. Lamberti^(a*), G. Berlier^(a*), G. Turnes Palomino^(a*), S. Bordiga^(a),
F. D'Acapito^(a*), E. Giamello^(a) and A. Zecchina^(a),

(a) Dipartimento di Chimica I.F.M., Via P. Giuria 7, I-10125 Torino, Italy

(b) INFM, c/o ESRF-GILDA CRG, ESRF, BP 220 F-38043 Grenoble, France

Report: During this experiment, a remarkable improvement of our experimental set-up has been performed. We have coupled our catalytic cell (*ad hoc* conceived for XAFS measurements allowing *in situ* thermal treatments, evacuation up to 10⁻⁴ Torr and gas dosage to be made) with the GILDA cryostat chamber. This allows measurements to be made in the 80-600 K interval and the exact and immediate location of the cell into the X-ray beam. In order to assure very high quality XANES spectra, the geometry of the beamline was optimized to improve the energy resolution: vertical slits, located at 23 m from the source, were set to 0.6 mm assuring at 9 keV, an actual energy resolution better than 0.5 eV. A 7 μm thick copper metal foil was put after the cell in order to collect an I₂ calibration spectrum (with a photodetector). This set-up avoids any problem related to little energy shifts due to small thermal instability of the monochromator crystals (the bottom inset of Fig. b reports 7 successive reference spectra). Fig. a) reports the XANES spectra collected on the Cu^{II}-ZSM-5 sample activated at increasing temperatures (from RT to 400 °C), while Fig. b) reports the effect of successive *in situ* dosage of H₂O and of H₂O/ O₂ mixture. The Cu^I ↔ Cu^{II} Red-Ox process is evident, as monitored by the evolution of both the dipole-allowed 1s → 4p transition of Cu^I ions, at 8983 eV and the weak quadrupole 1s → 3d absorption at about 8977.5 eV. The EXAFS data analysis show that, after activation at increasing temperature, a dramatic reduction of the Cu-O coordination number (from 3.9 ± 0.4 to 2.3 ± 0.3) occurs, correlated with a small increment of the first shell the Cu-O bond distance (from 1.94 ± 0.02 Å up to 1.98 ± 0.02 Å). These XAFS data, supported by parallel EPR, IR and UV-Vis are discussed in detail in Ref. [1]. Fig. c) reports the evolution of the pre-edge region upon *in situ* formation of well-defined Cu^I(CO), Cu^I(CO)₂ and Cu^I(CO)₃ complexes (the first two at RT, the last at 80 K). These data give new information on the study of the σ- donation and π-back-donation processes involved in the copper carbonyl formation, deeply discussed in Ref. [2]. Fig. d) reports the effect of the displacement of a CO ligand by *in situ* dosage at 80 K of NH₃ on preformed tricarbonyl complexes giving rise to the formation of Cu^I(CO)₂NH₃ mixed complexes inside the ZSM-5 channels [2]. The quality of the XANES spectra collected at the ESRF during this experiment is remarkably high (as was that of exp. CH-132 [3]), and by comparing them to those collected by us at LURE on similar Cu-zeolites [4] we can conclude that the use of ESRF source has been indispensable to observe so fine but important features in the XANES spectra.

[1] P.Fisicaro, G. Turnes Palomino, E. Giamello, S.Bordiga, C.Lamberti, A.Zecchina, *J. Am. Chem. Soc.* submitted.
 [2] A.Zecchiana, S.Bordiga, G.Spotto, D.Scarano, C.Lamberti, M.Salvalaggio, *J. Phys. Chem. B*, **103** (1999) in press.
 [3] C.Lamberti et al, *Chem. Phys. Lett.* **269** (1997) 500; *J. Phys. IV France*, **7** (1997) C2-903.
 [4] C. Lamberti et al. *J. Phys. Chem. B*, **101** (1997) 344; *J. Chem. Soc. Faraday Trans.*, **94** (1998) 1519.

