ESRF	Experiment title: Study of the aggregation and reduction of Ag^I counterions in Ag^I-ZSM-5, Ag^I-Y and Ag^I-MOR as a function of the activation conditions by means of XAFS and anomalous XRD	**Experiment number:** **CH-377**
Beamline: **MB29**	**Date of experiment:** from: 17/09/1997 to: 20/09/1997	**Date of report:** February 10 1999
Shifts: **9**	**Local contact(s): Adriano FILIPPONI**	*Received at ESRF:* 0 1 MAR. 1999

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Report:

Proposal CH-377 was a combined XAFS/XRPD proposal: since no XRPD beamtime was allocated this is only a XAFS report. For brevity we will discuss only the Ag^+-ZSM-5, similar high quality XAFS data have been collected for Ag^+-MOR and Ag^+-Y. Ag^+-ZSM-5 has been prepared by ion exchange with an aqueous solution of $AgNO_3$ starting from the same NH_4-ZSM-5 sample (Si/Al= 14, kindly supplied by EniChem SpA, centro Ricerche di Novara) already used by us for a deep investigation of the Cu^+-ZSM-5 system [1]. This will allow us to do a deep comparison between the two similar systems. IR spectroscopy has evidenced that Ag^+-ZSM-5 has bean nearly totally exchanged (absence of any appreciable sign of the O–H stretching band of bridged Si-(OH)-Al groups), as was the case for Cu^+-ZSM-5 [1]. The cation exchanged zeolite powder has been divided into three sets. Care has been taken to prevent, as much as possible, exposure of the first set to light, since long exposures could lead to photoreduction of Ag^+ ions and formation of metal clusters. On the contrary, the second set has been exposed to an UV lamp for two days. As far as the third set is concerned, it has been thermally activated at higher temperature (673 K) for 2 hours. In such a way, an increasing percentage of Ag^I was reduced forming metal Ag^0 or charged Ag_n^{x+} (typically $2 < n < 50$ and $1 < x < 4$) nano-clusters trapped inside the zeolitic cages/channels. Our EXAFS data, qualitatively supported by parallel UV-Vis study, have shown that the aggregation process, is negligible for the first set of zeolite, small for photoreduced samples (5-10 %) and becomes consistent for thermally reduced samples (up to 40-50%). For Ag^+-MOR and particularly Ag^+-Y a measurable fraction of reduced silver was present also in the set of powder not exposed to light. EXAFS analysis has shown that the local environments of Ag^+ and Cu^+ ions in ZSM-5 is very similar, being Cu^+ surrounded by 2.5±0.3 oxygen atoms at 2.00±0.02 Å and Ag^+ surrounded by 2.5±0.4 oxygen atoms at 2.30±0.03 Å (Fig.1). Low temperature IR spectroscopy has shown formation of $M^+(CO)_n$ species where n= 1,2 for Ag^+ and n=1,2,3 for Cu^+. The same experiment, monitored by XAFS spectroscopy is reported in Fig.2 and 3 at a stage when only dicarbonyls are formed in the two systems. While $Cu^+(CO)_2$ forms an angle of about 130° [1], we have evidenced that $Ag^+(CO)_2$ forms an angle very close to 180°, giving so rise to the near co-linearity of 5 atoms (OC-Ag^+-CO) which enhance the multiple scattering contributions (see full line curve in Fig.3b) [2]. Results of this experiment are in press [3,4]. We thank the important and friendly support of Adriano Filipponi who has given us the opportunity to do a 3 h test 12 weeks before the experiment: this has allow us to optimize the beamtime during the experiment. We thank Dr. Moroni for having assured us to work under save conditions by kindly supplying the CO detector.

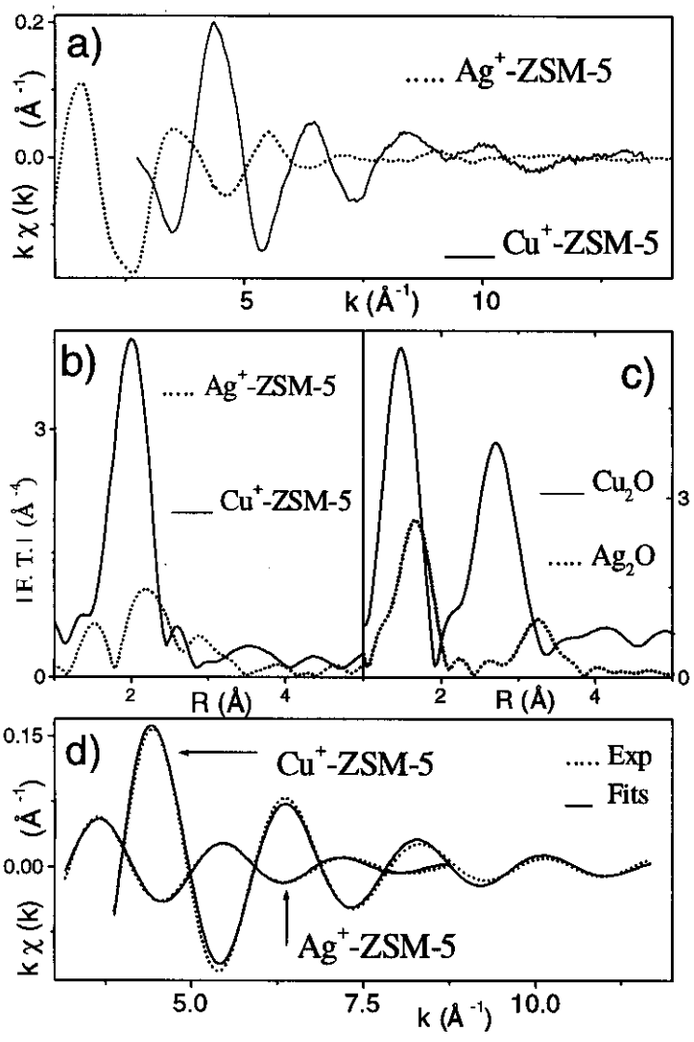

Fig.1 EXAFS results obtained on Cu^+-ZSM-5 and Ag^+-ZSM-5 samples. a) Experimental $k\chi(k)$ functions; b) k^3-weighted and phase corrected FT functions; c) same for the Ag_2O and Cu_2O model compounds but without phase corection; d) back-FT of the first shell filtered data for Ag^+-ZSM-5 and Cu^+-ZSM-5, and corresponding fits.

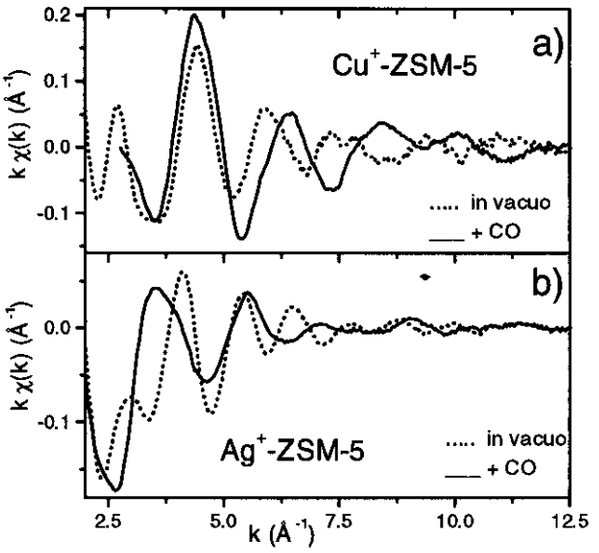

Fig. 2 Effect of CO dosage in k space: comparison between Cu- and Ag-ZSM-5

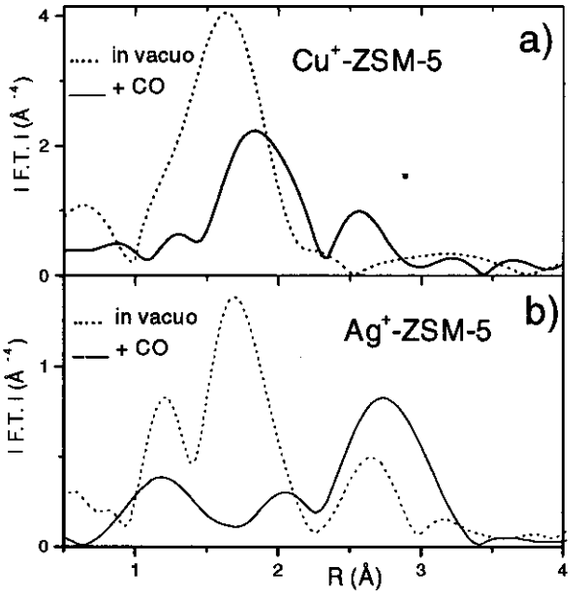

Fig. 3 Effect of CO adsorption in R space: comparison between Cu^+-ZSM-5, and Ag^+-ZSM-5 systems, parts a) and b), respectively.

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