

# Characterization of Binary Ag-Cu Ion Mixtures in Zeolites: Their Reduction Products and Stability to Air Oxidation

Steven Fiddy<sup>1</sup>, Vitalii Petranovskii<sup>2</sup>, Steve Ogden<sup>3</sup>, Inocente Rodríguez Iznaga<sup>4</sup>

<sup>1</sup> CCLRC Daresbury Laboratory, Daresbury, Warrington, UK, WA4 4AD

<sup>2</sup> CCMC-UNAM, Apdo Postal 2681, 22800 Ensenada. B.C., Mexico

<sup>3</sup> Department of Chemistry, University of Southampton, Southampton, UK

<sup>4</sup> Laboratorio Ingeniería de Zeolitas, Instituto de Materiales y Reactivos (IMRE) – Universidad de la Habana. Zapata y G. s/n. La Habana 10400. Cuba.

**Abstract.** A series of Ag<sup>+</sup>-Cu<sup>2+</sup> binary mixtures with different Ag/Cu ratios were supported on mordenite with different Si/Al ratios and were subsequently reduced under hydrogen in the temperature range 323K – 473K. Ag and Cu K-edge X-ray Absorption Spectroscopy (XAS) was conducted on these systems in-situ to monitor the reduction species formed and the kinetics of their reduction. In-situ XANES clearly demonstrates that the formation of silver particles is severely impeded by the addition of copper and that the copper is converted from Cu(II) to Cu(I) during reduction and completely reverts back to Cu(II) during cooling. There are no indications at any stage of the formation of bimetallic Ag-Cu clusters. Interestingly, the Ag/Cu ratio appears to have no influence of the reduction kinetics and reduction products formed with only the highest Si/Al ratio (MR= 128) investigated during this study having an influence on the reduction and stability to air oxidation.

**Keywords:** Silver-Copper clusters; Reduction; Oxidation; X-ray Absorption Spectroscopy; Mordenite

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## INTRODUCTION

The ability to synthesis and stabilize small metal clusters with precise control over both size and composition is a major challenge in catalysis. Main efforts have been directed towards the preparation of mono-metallic supported metal particles. Bimetallic systems have also become a hot topic recently where the properties of the system not only depend on particle size but particle composition as well. Generally, four types of structure would be expected for bimetallic particles: (i) a homogeneous solid solution of the metals; (ii) an intermetallic compound; (iii) nanoheterogeneous “core-shell” structures or (iv) aggregated nanodomains of individual metal clusters [1].

Zeolite-based materials are of great interest both from a practical and fundamental viewpoint in that they provide a unique host for various compounds, ultrafine particles, clusters, etc. The two most important features for the production of stable cluster-containing materials are: (i) the monosized voids in the crystal lattice and (ii) the amount of alkali-metal ions tolerated by the Si/Al ratio. We have already shown that under certain conditions the reduction of silver in zeolites can lead to the self-assembly and stabilization

of Ag<sub>8</sub> clusters [2] and that in separate experiments, the reduction of copper supported in zeolites can lead to a variety of different Cu species [2-4]. Some investigations have been conducted previously to characterize the structure of silica supported binary Ag-Cu clusters by EXAFS [5] which showed that there was extensive segregation of the components with the copper rich region in the interior of the clusters with the silver concentrated at the surface. The main aims of this present work are to investigate approaches to bimetallic Ag-Cu nanostructure formation inside the zeolite voids discovering what roles the addition of copper, the Ag/Cu ratio and the Si/Al ratio of the zeolite plays on the kinetics and products of hydrogen reduction and under air oxidation.

## EXPERIMENTAL

Ag<sup>+</sup> and Ag<sup>+</sup>-Cu<sup>2+</sup> binary mixtures with different Ag/Cu ratios were supported on mordenite with different Si/Al ratios (MR = 10, 30, 128). Mordenite was supplied by TOSOH Corporation, Japan. Ion exchange was carried out for one day from two component mixture of 0.1N water solutions of AgNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>, mixed in the ratios of 1:1 and 1:9 respectively. The excess of solution was removed and

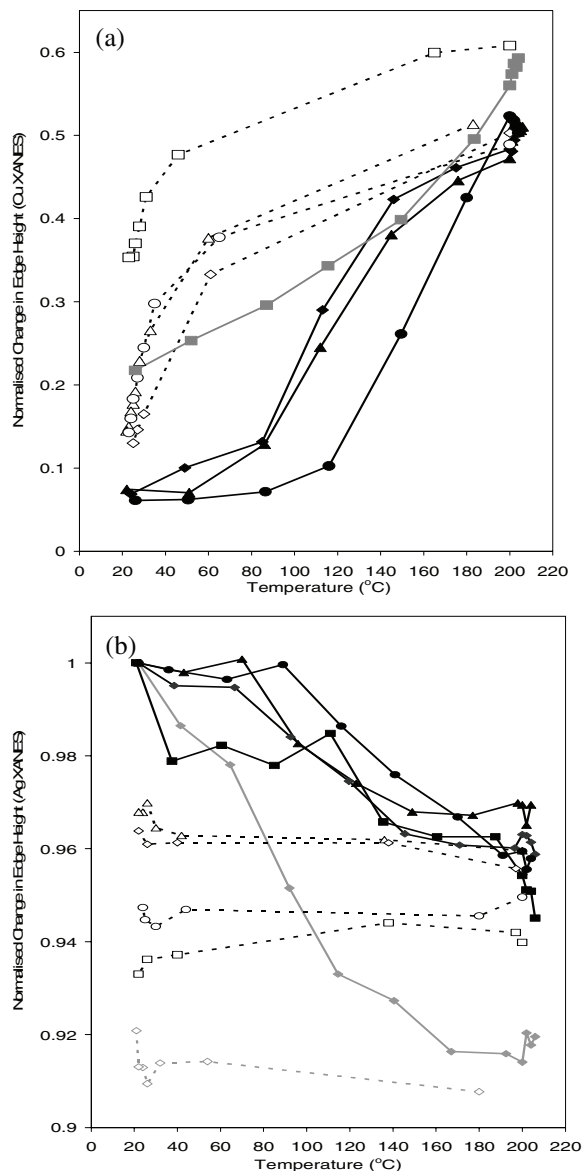
the samples washed and dried under ambient conditions. Throughout the text and figures, samples are abbreviated as AgCuM, accompanied by the value of nominal Si/Al and Ag/Cu ratio (e.g., AgCuM(10)-1:1).

X-Ray absorption spectroscopy measurements were performed on station 7.1 and 16.5 at the Cu and Ag K-edges respectively. The SRS operates with an average stored energy of 2GeV and a typical electron current of 200mA. Both stations are equipped with a harmonic rejection, double-crystal monochromator (Si(111) for 7.1 and Si(220) for 16.5), the second crystal of which allows sagittal focusing of the X-ray beam. Harmonic rejection was set to 70% for both edges. Data was collected in transmission mode at the Ag K-edge and in fluorescence mode for the Cu K-edge. For the in situ experiments, a glass reactor cell with Kapton windows to allow X-rays access/egress was used. Pellets were prepared by pressing the powdered sample materials without the addition of an external diluent. The pellets were placed into the reactor cell and were heated up to 473K at 5Kmin<sup>-1</sup> under dry 10% H<sub>2</sub>/N<sub>2</sub>. During all experiments, data was also measured simultaneously for the appropriate metal foil placed between the second and third ion chambers to provide an edge shift calibration for the XANES data. For all oxidized samples, these were recorded after one week exposure to air at ambient temperature and pressure. Typically for the EXAFS spectra, 4 scans at the Ag K-edge and 6 scans at the Cu K-edge were collected and summed prior to curve fitting. Background subtracted EXAFS data were obtained using the programme PAXAS[6]. Spherical wave curve fitting analysis was executed in EXCURV98[7], using ab initio phase shifts and backscattering amplitudes calculated using Von-Barth ground state potentials and Hedin-Lundqvist exchange potentials. The R-factor is defined as  $(\int [\chi^T - \chi^E] k^3 dk / \int [\chi^E] k^3 dk) \times 100\%$  where  $\chi^T$  and  $\chi^E$  are the theoretical and experimental EXAFS and  $k$  is the photoelectron wave vector. Where the size of the Ag cluster (number of silver atoms) is reported in relation to the 1<sup>st</sup> shell CN, the theories and method evaluated by Jentys was used [8].

## RESULTS AND DISCUSSION

Initially, a pure AgM(10) sample was reduced to provide a reference from which the effects of copper addition could be investigated. Figure 1(b) shows the change in the edge height during the reduction procedure and clearly showed the transformation of Ag(I) to Ag(0) as indicated by the decrease in the white line (recorded at 25525eV). On cooling, it was noted that there was minimal reversibility in this process and the Ag species formed at 473K remains

stable. Even after oxidation in air for one week, no changes in the XANES spectra were observed.



**FIGURE 1.** Changes in the (a) Cu and (b) Ag XANES for AgM(10) (grey diamonds), AgCuM(10)-1:1 (triangle), AgCuM(10)-1:9 (diamond), AgCuM(30)-1:1 (circle), and AgCuM(128)-1:1 (square) during heating (solid) and cooling (dotted).

The EXAFS also follows this trend and is consistent with the formation of silver particles on reduction. In all cases, two main peaks are prominent in the Fourier Transform which are proposed to be due to the framework oxygens of the mordenite and the formation of Ag-Ag particles and clusters on and within the mordenite. Four main points can be concluded from these studies: i) the oxygen

**TABLE 1.** Ag K-edge  $k^3$ -weighted EXAFS derived structural parameters for Ag-Cu samples recorded during reduction and oxidation. In all the AgCu cases, the Debye-Wallers have been fixed for a particular treatment derived from analysis of the silver only catalyst (see table) and the coordination number refined to demonstrate the size of the clusters formed relative to the AgM catalyst. For Ag K-edge spectra, AFAC = 1.0 and  $\Delta k = 2.8 - 10 \text{ \AA}^{-1}$ . Errors in coordination number (CN) should be considered in the range  $\pm 10$ -20%, those of bondlengths ( $r$ )  $\pm 1.5$ -2%

Material	Treatment (Recorded at)	Atom Type	CN	Distance ( $\text{\AA}$ )	Fixed Debye-Waller Factors ( $\text{\AA}^2$ )	R-factor (%)
AgM(10)	200°C under $\text{H}_2/\text{N}_2$	O	1.1	2.321	0.022	43.9
		Ag	2.3	2.709	0.029	
	Room Temp under $\text{H}_2/\text{N}_2$	O	1.0	2.347	0.019	25.3
		Ag	5.7	2.852	0.026	
	Room Temp in air	O	1.0	2.336	0.026	34.0
		Ag	5.7	2.864	0.027	
AgCuM(10)-1:1	200°C under $\text{H}_2/\text{N}_2$	O	1.1	2.332	0.022	43.9
		Ag	1.8	2.717	0.029	
	Room Temp under $\text{H}_2/\text{N}_2$	O	1.5	2.307	0.019	32.9
		Ag	1.7	2.742	0.026	
	Room Temp in air	O	2.2	2.319	0.026	25.5
		Ag	1.6	2.763	0.027	
AgCuM(10)-1:9	200°C under $\text{H}_2/\text{N}_2$	O	1.1	2.355	0.022	36.2
		Ag	1.9	2.754	0.029	
	Room Temp under $\text{H}_2/\text{N}_2$	O	1.4	2.334	0.019	33.5
		Ag	1.9	2.768	0.026	
	Room Temp in air	O	2.2	2.331	0.026	21.9
		Ag	1.5	2.770	0.027	
AgCuM(30)-1:1	200°C under $\text{H}_2/\text{N}_2$	O	1.3	2.342	0.022	28.3
		Ag	1.9	2.699	0.029	
	Room Temp under $\text{H}_2/\text{N}_2$	O	1.5	2.317	0.019	25.1
		Ag	1.9	2.719	0.026	
	Room Temp in air	O	2.0	2.317	0.026	21.8
		Ag	2.4	2.769	0.027	
AgCuM(128)-1:1	200°C under $\text{H}_2/\text{N}_2$	O	1.2	2.342	0.022	36.7
		Ag	1.8	2.697	0.029	
	Room Temp under $\text{H}_2/\text{N}_2$	O	1.5	2.299	0.019	40.1
		Ag	1.5	2.727	0.026	
	Room Temp in air	O	1.9	2.325	0.026	51.7
		Ag	3.3	2.803	0.027	

contribution remains even at 473K suggesting that the oxygens are not due to hydration, (ii) unlike previous studies conducted on similar materials [9], no long Ag-O distances could be fitted to the data, (iii) the EXAFS indicates the formation of large silver particles ( $1^{\text{st}}$  shell CN  $\sim 6$  which relates to ca. 25 atoms and (iv) exposure of this sample to air causes no significant changes in the EXAFS environment suggesting that this species is stable towards air oxidation. For all materials studied, the Ag-Ag distance is lower than that observed for bulk silver ( $\sim 2.89 \text{ \AA}$ ) and is related to the higher electron density between atoms because of the dehybridisation of the spd metal orbitals [10].

Next the addition of copper was investigated by characterising the kinetics of reduction and the species formed after oxidation and reduction for AgCuM(10)-1:1. From the changes during the Ag XANES (and the comparison with the pure AgM(10) materials), it can quite clearly be seen that although reduction has occurred for the AgCu material, the decrease in edge

height is considerably smaller than that observed for the AgM(10) material. If the Cu XANES is also investigated over the same temperature range, it demonstrates the very clear growth of a pre-edge feature (centred around 8980eV) which has been assigned to the formation of Cu(I) due to the reduction of Cu(II). Initially, the reduction parameters of AgM and AgCuM appear very similar – however, by ca. 453K, when the Cu(I) feature starts to develop, there is minimal change in the Ag XANES demonstrating that Cu is impeding particle information during the reduction procedure itself. Also, it should be noted that on cooling to room temperature, there is completely reversibility with no obvious indications of retention of the Cu(I) or disproportionation to Cu(II) and Cu(0).

The XANES interpretation is also confirmed by analysis of the EXAFS data (Table 1) which suggests that only very small silver clusters are formed ( $1^{\text{st}}$  shell CN  $\sim 2$  relating to clusters of ca. 4-8 atoms) when the Cu is added. Importantly on cooling, the size of the

cluster remains about the same with no indication that at room temperature or after oxidation in air that the Ag cluster are completely oxidised to reform monatomic species. The lack of any obvious features at higher distances in the Fourier Transform, which would represent some degree of long range structure for these silver clusters, is also minimal also providing further evidence as to the small size of these Ag clusters. Interestingly, even though the copper does play a significant role in the Ag reduction kinetics and final species, there is no evidence from either the Ag or Cu EXAFS that there is any formation of bimetallic clusters or alloying. Therefore, at this present time, it is unclear how the copper impedes the formation of the bigger silver particles but reasons may include spatial impedance (i.e. Cu more strongly bound to the zeolite thereby restricting movement over the zeolite surface) or electronic impendence.

Two other parameters (namely the Ag/Cu and the Si/Al ratio) were also manipulated to see if either of these had a significant impact on the reduction procedure or oxidation characteristics of these materials. Figure 1(a) and (b) show the change in edge height for the Ag XANES and Cu pre-edge feature for a lower Ag/Cu ratio (1:9) and for two other Si/Al ratios (30 and 128). As can be seen from the two figures, the change in the Ag/Cu ratio makes little or no difference to the reduction kinetics of these materials. This is also demonstrated by analysis of the EXAFS data for this material in which the coordination numbers and distances are almost exactly identical to that observed for the 1:1 ratio material (Table 1).

Comparing the XANES for the three different Si/Al ratios, it is evident that there is little influence on the reduction kinetics until the highest ratio is reached. Two important observations can be drawn for the Si/Al = 128 material; (i) even at room temperature, the height of the pre-edge feature in the Cu XANES is larger relative to the height observed for the other materials. This suggests that there is a higher percentage of Cu(I) in this material before heating even occurs and concurrently, there is a higher percentage of Cu(I) after reduction and cooling relative to the other systems. This also appears to have some influence on the silver species formed with a reduction in the Ag-Ag coordination number in comparison with the other systems (ii) the species observed after air oxidation demonstrates different degrees of reduction which can be correlated to the Si/Al ratio. The initial species for all samples instantly after reduction at room temperature are all very similar – however, it appears that the higher the Si/Al ratio, the greater the degree of reduction the Ag appears to undergo in air. This is not completely surprising as it has previously been demonstrated that for the Ag

clusters, the stability of the clusters decreases with acid site strength that in turn depends on the Si/Al molar ratio [11]. However, in that case, it was found that the higher Si/Al ratios destabilized the clusters and oxidized them to Ag ions. What is unusual in the present situation is that the Ag-Ag interactions appear to increase from a low starting Ag-Ag coordination number for the higher Si/Al ratios. Further work is currently in progress to explain what mechanism is operating for these materials.

## CONCLUSIONS

The addition of copper to these materials considerably impedes the formation of large Ag particles during the reduction procedure itself causing the formation of significantly smaller Ag clusters. It should also be noted that a reduction from Cu(II) to Cu(I) occurs upon heating which is completely reversible upon cooling (which is proposed to have significant bearing on the Ag cluster/particle formation). At no stage are there any indications of bimetallic clusters suggesting that Ag and Cu have a mutual influence due to their concurrence for ion-exchange sites and relative positions in the mordenite voids. Additionally, it also appears that the Ag/Cu ratio has little influence on the reduction procedure with only the highest Si/Al ratio having any significant influence on the reduction and oxidation species.

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