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EXAFS and optical spectroscopy characterisation of reduction products of binary silver-copper ion mixture in mordenite

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Abstract. Ag^+, Cu^{2+} and $Ag^+ - Cu^{2+}$ binary mixtures with different Ag/Cu ratios were supported on mordenite with Si/Al ratio equal to 10 and reduced in the temperature range 323−673 K. Diffuse Reflectance UV-Visible spectra reveal appearance of Ag_8 clusters and small copper metal particles. Cu K-edge EXAFS show for Cu-rich non-reduced samples the presence of only oxygen shell; but for the Ag-rich sample, the presence of heavier backscatterer is also indicated producing a different EXAFS envelope. Silver EXAFS analysis suggests that, for the reduced samples, there are both $Ag - O$ and $Ag - Ag$ distances ($Ag - Ag$ and $Ag - O$ coordination numbers of approx 2 and of 1.3 respectively for the Ag/Cu = 3:1 and 1:3 samples). Importantly, for the reduced sample, the EXAFS indicates that Ag appears to promote/stabilise Cu cluster formation whereas Cu appears to impede/destabilise Ag cluster formation.

PACS. 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc. – 36.40.Vz Optical properties of clusters – 82.75.Vx Clusters in zeolites

1 Introduction

The ability to synthesize nanoparticles with precisely controlled size and composition and the assembly of them into larger structures with unique properties is one of the great challenges. Nanosize metal particles are intermediate between the bulk metals and individual atoms, being of considerable theoretical and practical interest. Main efforts are directed on the preparation of mono-metal supported nanoparticles. Recently papers concerning bimetallic system formation began to appear [1–5]. The properties of such kind of systems depend not only on the particle composition, but on the particle structure as well. Four types of structures would be expected for bimetallic particles: it might be (i) a homogeneous or nearly homogeneous solid solution of the metals; (ii) an intermetallic compound; (iii) nanoheterogeneous “core-shell” structures or (iv) aggregated nanodomains of individual metal clusters [1].

Zeolites are an example of ordered nanoporous materials with regular pores that are able to incorporate different species and regularly arrange them inside the intracristalline space. It was shown previously that reduction of Ag-mordenites under certain conditions leads to self-assembling of Ag_8 clusters [6]. More complicated chemistry was demonstrated by Cu-mordenite samples, leading to formation of different kind of Cu reduced species [6–8]. The $Cu - Ag$ system was selected because both metal clusters are known to be promising $de - NO_x$ catalysts [9–12]. Ag-mordenite and Cu-mordenite systems were carefully studied earlier [6–8,13,14]. Thermodynamic properties of the $Cu - Ag$ system are well-known [15]. Some attempts to investigate structure of non-equilibrium silica-supported binary $Ag - Cu$ clusters were done using extended X-ray absorption fine structure (EXAFS) [16]. The atomic ratio of copper to silver was close to one in the material investigated in that work. The EXAFS results, which were obtained in the presence of hydrogen, indicate extensive segregation of the components in the silver-copper clusters. This pronounced segregation is readily understandable, since silver and copper are only slightly miscible in the bulk. The EXAFS results on the silver-copper clusters suggest that the copper-rich region is in the interior of the clusters, with the silver concentrating at the surface [16]. The aim of the present work is to investigate experimentally approaches to bimetallic $Ag - Cu$ nanostructure formation inside the zeolite voids.

2 Experimental

Ag^+, Cu^{2+} and $Ag^+ - Cu^{2+}$ binary mixtures with different Ag/Cu ratios were supported on mordenite with Si/Al

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Table 1. Cu and Ag content (wt%) and observed Ag/Cu atomic ratio of the samples under study.

Sample	Ag	Cu	Ag/Cu$_{nominal}$	Ag/Cu$_{observed}$
CuM [7]	-	1.0	-	-
AgM [13]	1.0	-	-	-
AgCuM(3:1)	8.0	1.4	6:1	3.7:1
AgCuM(1:3)	4.9	1.5	0.7:1	2:1
AgCuM(1:9)	2.2	1.5	0.02:1	1.1:1

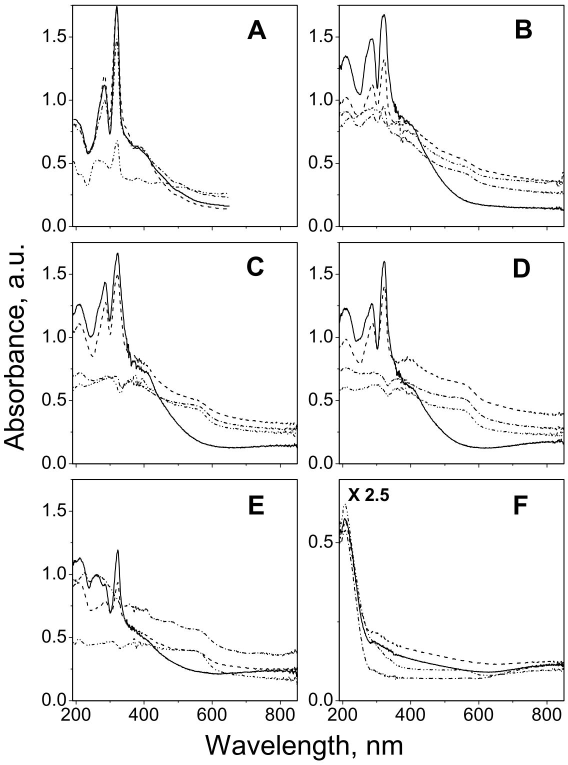

Fig. 1. DRS spectra of samples AgMor (A), AgCuM(3:1) (B), AgCuM(1:1) (C), AgCuM(1:3) (D), AgCuM(1:9) (E) and CuM (F) reduced at 100, 200, 300 and 400 °C (solid, dash, dash-dot and dash-dot-dot lines respectively). Scale of entrance (F) is multiplied by factor 2.5.

ratio equal to 10. Mordenite was supplied by TOSOH Corporation, Japan. Ion exchange was carried out for one day from two-component mixture of 0.1 N water solutions of $AgNO_3$ and $Cu(NO_3)_2$, mixed in ratios 3:1, 1:3 and 1:9 respectively, thus saving the total normality of the mixed solution. The excess of solution was removed; samples were washed and dried under ambient conditions followed by heating in dry H_2 flow in the temperature range 100−400 °C for 4 h. Throughout the text and figures, samples are abbreviated as AgCuM, accompanied by the value of nominal Ag/Cu ratio and temperature of the hydrogen reduction in °C, if applicable (*e.g.*, AgCuM(1:3)–200). The Ag and Cu content in the obtained samples was determined by a JEOL 5200 scanning electron microscope equipped with a Kevex Super Dry energy disperse spectroscopy (EDS) attachment. Quantification was done using the standard Magic 5 software. Diffuse reflectance spectra (DRS) were collected on a Varian Cary 300 spectrophotometer equipped with a standard diffuse reflectance unit. Ag and Cu K-edges EXAFS data were collected using the synchrotron source at Daresbury, UK.

3 Results and discussion

Monometallic Ag-Mordenite and Cu-Mordenite with the same Si/Al ratio studied in the previous works [7,13] after similar ion-exchange treatment adsorb approximately 1 wt% of the Ag and Cu. Samples obtained in the course of the present work surprisingly demonstrate much higher degree of ion exchange. Results of analysis are shown in the Table 1. Also, note the significant deviations from nominal Ag/Cu atomic ratios refer to observed ones. Copper adsorption seems to be constant, while silver is adsorbed more and more selectively with decreasing its content in the mixture.

Drastic changes in the conditions of Ag_8 cluster formation and their relative stability in the binary mixtures were observed. The reduced Ag appears in the UV-Vis range as absorption maxima 295 and 320 nm (Fig. 1), assigned to Ag_8 clusters [6,14]; this assignment was confirmed by EXAFS study [17]. For lower Ag/Cu ratios, the relative intensity of the 295 nm peak diminishes and finally disappears, while the 320 nm peak is still present up to the highest temperatures applied. The plasma resonance peak, connected with the formation of Ag nanoparticles was not observed. In contrast, for Ag-mordenite, both the 295 and 320 nm peaks appears and disappears simultaneously with the changing of the reduction conditions; plasma resonance peak appears under high temperature reduction. The effect of Ag upon the plasmon resonance band (560−600 nm) and other lower-wavelength bands associated with the reduced Cu species were well pronounced too. Ag addition assists the stabilization of Cu^+-ions (band at 250 nm) and the appearance of small Cu particles at significantly lower temperatures compared to pure Cu-mordenite. The cross-impact of Cu and Ag ions during reduction leads to the appearance of mixture of definite reduced species of Cu and Ag. Synergetic effects consist in the changing of the reduction temperature of Ag and Cu, as well as changing the stability of some reduced species and their relative concentration.

Formation of mixed Ag – Cu species cannot be concluded from the optical data obtained. The study of the bimetallic particle sols, produced by co-reduction of respective ions, shows a shoulder-like fall-off in the 450−600 nm wavelength region instead of the pronounced absorption bands characteristic of the individual copper and silver particles, indicating the bimetallic nanoparticles formation [18]. In our case, the only features in the spectra are the bands belonging to the individual silver and copper reduced species that can be obtained in the AgM and CuM independently [6,14].

From the Cu K-edge EXAFS (Fig. 2), it appears that the ratio of Ag/Cu makes very little difference to the

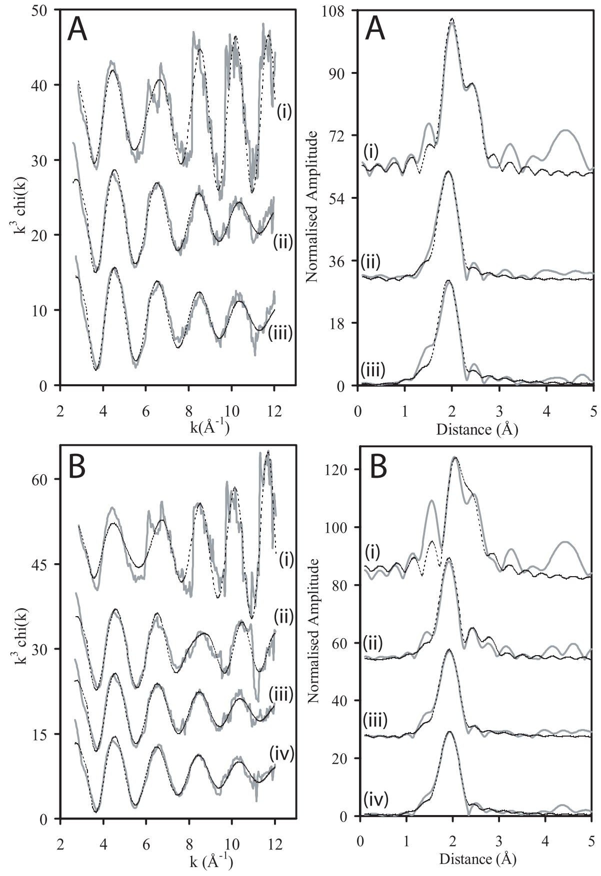

Fig. 2. Cu K-edge EXAFS and Fourier transform of non-reduced (A) and reduced (B) samples; (i) AgCuM(3:1) reduced at 100 °C, (ii) AgCuM(1:3) reduced at 100 °C, (iii) AgCuM(1:9) reduced at 100 °C and (iv) AgCuM(1:9) reduced at 200 °C. Solid grey line is experimental data, dash black line is theoretical data.

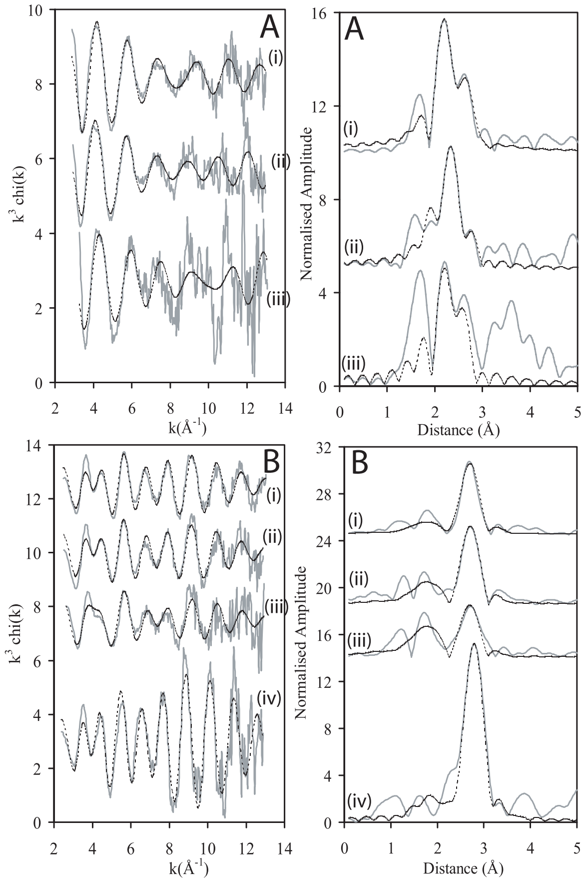

Fig. 3. Ag K-edge EXAFS and Fourier transform of non-reduced (A) and reduced (B) samples; (i) AgCuM(3:1) reduced at 100 °C, (ii) AgCuM(1:3) reduced at 100 °C, (iii) AgCuM(1:9) reduced at 100 °C and (iv) AgCuM(1:9) reduced at 200 °C. Solid grey line is experimental data, dash black line is theoretical data.

environment of the copper until a ratio of Ag/Cu = 3 is reached. At this point, there is a significant change in the both the EXAFS (a drastic change in the amplitude of the EXAFS at high k) and the Fourier transform (the appearance of a shoulder at 2.25 Å). It is hypothesised that this is due to the presence of a heavier scatterer, however the distance of 2.25 Å is very short for a direct covalent Cu – Cu or Cu – Ag bond. It is therefore suggested that the shoulder is caused by a unusual interference pattern between the two copper contributions (*i.e.* Cu – O and Cu – Cu or Cu – Ag).

From the Ag K-edge EXAFS (Fig. 3), it appears that if the Ag/Cu ratio is increased there is a higher contribution of oxygen neighbours and a decrease in the contribution of heavy backscatterer neighbours. One obvious explanation for this is that the Cu ions have a higher affinity for the ion exchange positions in the mordenite than the Ag ions, so if the Ag/Cu ratio is high Ag ions will sit preferentially in the ion exchange sites (an oxygen environment).

However, if the Ag/Cu ratio is low, Cu ions will preferentially fill the majority of ion exchange sites and the silver will be sited in other places within the mordenite, possibly as a $Ag^+ - Cu^{2+}$ ion pair.

From the Cu K-edge EXAFS, there are significant differences in the copper environment for the three different Ag/Cu ratios characterized (Fig. 2). For the lowest Ag/Cu ratio, the copper environment can be based on a simple oxygen model (4 oxygens at 1.973 Å), suggesting that the copper is found as copper ions (Cu^{2+}) with no obvious signs of clustering or particle formation. Interestingly, this simple oxygen model also holds true for the highest reduction temperature situation (200 °C). However, for the intermediate Ag/Cu ratio, both the EXAFS and Fourier transform change significantly (*i.e.* an increase in amplitude of the EXAFS at high k and the appearance of two peaks at 2.40 Å in the Fourier transform). Both of these changes suggest the presence of a heavier backscattering atom, and consequently clustering of the copper. Finally at the highest Ag/Cu ratio, the EXAFS and FT change again with a dramatic increase in the amplitude of the EXAFS at higher k. This suggests in this case, that there is a very high proportion of Cu clustering present. Three hypotheses have been put forward to explain this trend:

(a) the increase in silver content allows the formation of bimetallic Ag – Cu clusters, which can be formed at lower temperatures and are stable to air oxidation;
(b) in some fashion, the silver promotes the formation of Cu – Cu bonds during reduction and consequently, promotes Cu cluster formation;
(c) the addition of Ag prevents the oxidation of the copper species and hence increases their stability.

From the Ag K-edge EXAFS, it appears the addition of Cu either helps to produce smaller Ag clusters or promotes the oxidation of Ag clusters (Fig. 3). For the pure Ag mordenite sample reduced at 100 °C, the average Ag environment is 2.0 oxygens at 2.34 Å and 3.6 Ag at 2.83 Å. Both the Ag/Cu ratio of 3:1 and 1:3 can be fitted to very similar models (1.3 oxygens at 2.34 Å and 2.0 Ag at 2.77 Å) suggesting that the addition of Cu down to a Ag/Cu ratio of 1:3 produces no additional increase in the stability.

A significant retardation in the coordination of the Ag – Ag shell is observed, with an increase in Ag – O contributions for the smallest Ag/Cu ratio (1:9). This is important as it suggests that the addition of a high proportion of copper either decreases the ability of the silver to reduce thereby preventing the formation of clusters or facilities the air oxidation of the silver clusters formed. Another hypothesis that has been considered for these samples is the formation of Ag – Cu clusters, however fitting of the Ag K-edge EXAFS with copper shells rather than silver shells only produce a worse fit to the data and a higher *R*-factor. The trend observed in the Ag EXAFS is interesting and important because from the Cu EXAFS, the trend is reversed for the copper species formed. For example, at high Ag/Cu ratio (3:1), the formation of copper cluster species is promoted during reduction or is stabilized to air by the addition of silver, however the copper decreases the propensity of the silver to reduce or increases the propensity to oxidize. There appears to be a mutual effect between the silver and copper. It is unclear at present how this is achieved, however EXAFS analysis of both metals suggests that it is not due to a direct interaction between Ag and Cu.

Finally, higher reduction temperatures produce bigger clusters (best model to the EXAFS data contains 1.5 oxygens at 2.40 Å and 3.3 silvers at 2.85 Å), similar to those characterized for the pure Ag mordenite reduced at a lower temperature of 100 °C (best model to the EXAFS data is 2.0 oxygens at 2.34 Å and 3.6 oxygens at 2.83 Å). The coordination numbers and distances between the two samples are of comparable value.

4 Conclusions

Variations of the Ag/Cu ratio and reduction temperature influence the appearance of silver and copper reduced species. They were detected by means of optical absorption using diffuse reflectance spectroscopy technique as the characteristic peaks of size selected Ag_8 clusters and plasmon resonance band of copper nanoparticles. Changes in the temperature range of appearance and disappearance of distinct copper and silver species and variations of their relative stability were revealed. Formation of bimetallic particles was not detected. The observed effects are interpreted as a mutual influence of silver and copper ions and reduced species of silver and copper due to their concurrence for ion-exchange sites and relative positions in mordenite voids, respectively.

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