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Structure of silver clusters embedded in erionite channels

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Abstract. The structure of silver clusters stabilised in erionite has been studied by EXAFS, and the results support an interpretation given previously that the absorption peaks at 322 and 293 nm in the optical spectra of the sample belong to the cluster species Ag_8^0 and $Ag_8^{\delta+}$. Five possible geometries were considered for an Ag_8 cluster, and for each one, the expected Ag EXAFS was calculated and compared with the experimental data. The observed coordination numbers indicate an absence of bulk silver metal, and the best fit was obtained for a polyhedron with D_{2d} symmetry, which corresponds closely with the results of minimum energy structure calculations. The derived Ag−O distances discount the formation of silver oxides, but are consistent with a weak interaction between the silver clusters and the oxygen atoms of the surrounding channel. The results therefore indicate that erionite promotes the formation of 8-atom silver clusters in the channels of the crystalline framework.

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1 Introduction

It has previously been shown that silver clusters in solution, which are characterised by a peak at 320 nm in the optical spectrum, are unusually long-lived [1]. Their life-time in solutions without any ligand stabiliser is typically about 10 min, and significantly exceeds the life-time of other kinds of silver clusters in these systems. However, the life-time of the silver clusters inside zeolites can be much longer (days or months) [2]. According to kinetic data obtained in solution, and spectroscopic data obtained for mass-selected silver clusters stabilised in inert gas matrices, the peak at 320 nm may be assigned to clusters Ag_8 [1, 3]. The same absorption peak at 320 nm is observed in the spectra of silver clusters trapped in mordenites exhibiting a wide range of composition (e.g. SiO_2/Al_2O_3 molar ratios from 10 to 206) [4, 5]. The similarity between the optical spectra of silver clusters in solutions, inert gas matrices and zeolites suggests that it is predominantly 8-atom silver clusters, which are stabilised in zeolites. The life-time of the clusters in mordenite is typically a factor of 10^4 longer than in solution [5].

Mordenite represents a two-dimensional system of crossing channels, which are characterised by different elliptic cross-section with axes: (a) 0.29–0.57 nm; (b) 0.67 – 0.70 nm [6]. Erionite has elongated cavities with diameter 0.63 nm and length 1.5 nm connected by small windows with a diameter 0.25 nm. The cavities of neighbouring channels are interconnected with twisted 8-member rings (with sizes 0.36×0.52 nm) [6]. The existence of the cavities isolated by the narrow windows in erionite could lead to an increase in stability compared with silver clusters in mordenite.

Erionite is characterised by a significantly (×4) lower SiO_2/Al_2O_3 molar ratio, so the cation concentration in erionite framework is 4 times higher than in mordenite and consequently, the silver concentration in erionite is expected to be higher than in mordenite. In addition, the application of K,Na-form of erionite could also increase the silver cluster concentration compared with protonated mordenite since cation exchange occurs easier with alkali metal forms than with a protonated form [6].

In the present work silver clusters in erionite, with a high silver concentration and a long life-time, were prepared and silver *K*-edge EXAFS studies were performed to establish the geometrical structure of these clusters.

Five possible models for Ag_8 were considered, and for each one the calculated EXAFS is compared with

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[b] It is with great sadness that we report the death of Dr. J.M. Corker (July 10th 1998).

the experimental Ag K-edge data. However, only one of these showed good agreement between theory and experiment.

2 Experimental section

In this work an erionite sample with SiO_2/Al_2O_3 molar ratio 7.7:1 and containing 11.2 wt. % K_2O and 2.4 wt. % Na_2O were used. For Ag-erionite sample preparation, the same technique as for Ag-mordenite samples [5] was used. Silver ion exchange was carried out from 0.1 N $AgNO_3$ water solution for 3 days. The excess of solution was removed, samples were dried in vacuum at ~ 345 K and then heated in a H_2 flow at 373 K for 4.5 h. The silver content measured using an X-ray Fluorescence Spectrometer SEA 2010 was 14 wt. %.

Diffuse reflectance UV-Vis. spectra were recorded under ambient conditions on a Perkin Elmer 330 spectrometer with a standard diffuse reflectance unit, using undoped erionite as a reference.

Silver K-edge EXAFS data were collected using the synchrotron source at Daresbury, UK, operating at 2 GeV, and samples were studied in both transmission and fluorescence mode, with data sets extending to typically to $k = 14\,\text{Å}^{-1}$. The Ag edge position was calibrated using silver foil, and background subtractions were carried out using standard polynomials within the program PAXAS [7]. Subsequent curve-fitting utilised the single scattering curved wave theory incorporated in EXCURVE, with phaseshifts and backscattering factors calculated by normal ab initio methods [8].

3 Results and discussion

The diffuse reflectance spectra of Ag-mordenite [5] and Ag-erionite in the UV region are very similar (Fig. 1). Two peaks, at 322 and 293 nm for Ag-erionite and 320 and 283 nm for Ag-mordenite, are observed. Both peaks are attributed to 8-atom clusters (Ag_8^0 and $Ag_8^{\delta+}$) [1, 3, 5]. The two peaks observed in the visible region of the spectrum for Ag-erionite will be discussed below.

The positions of the absorption peaks of Ag_8 clusters are slightly different in different media [1, 3, 5]. In aqueous solutions two peaks at 325 and 295 nm are observed [1]. The positions of these peaks are very close to ones observed for Ag-erionite (322 and 293 nm). The peak of mass-selected Ag_8 clusters in solid argon is observed at 319 nm [9]. The matrix effect on peak position can be illustrated by the example of mass-selected Ag_7 clusters embedded in solid inert gases where a shift ca. 20 nm was observed due to the change of matrix from argon to xenon [9]. This shift results from the difference in the dielectric constants of solid argon and xenon.

The matrices used in the present work have different chemical compositions. Erionite contains 13.6 wt. % of alkali metal oxides while mordenite is used in the protonated form. In addition, SiO_2/Al_2O_3 molar ratios of erionite and mordenite differ and are 30:1 and 7.7:1, respectively. Finally, the pore geometries for these matrices are different. Erionite has elongated cavities, and mordenite channels have no windows, but are characterised by a elliptic cross-section. Taking into account these differences between the composition and pore geometry of mordenite and erionite matrices the observed shift ca. 10 nm of shorter wavelength peak (283 nm to 293 nm) seems to be reasonable.

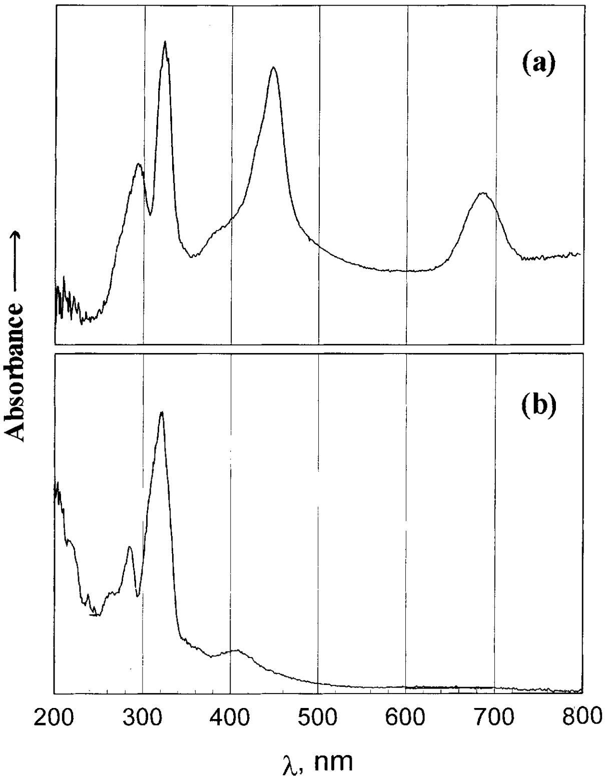

Fig. 1. Diffuse reflectance UV-Vis. spectra of samples prepared at 373 K: (a) Ag-erionite (14 wt. % of Ag; SiO_2/Al_2O_3 molar ratio 7.7:1); (b) Ag-mordenite (0.66 wt. % of Ag; SiO_2/Al_2O_3 molar ratio 30:1) [5].

The cluster peaks of Ag-erionite did not change for more than four years in contrast to those of Ag-mordenite, where decomposition could be observed after as little as two weeks [5].

The Fourier transform of the raw EXAFS data showed essentially two shells, arising from Ag−O and Ag−Ag distances, and after applying standard phaseshift corrections these corresponded to 2.30 and 2.77 Å, with average coordination numbers of 2 and 1 respectively. In metallic silver, the first (Ag−Ag) shell lies at 2.89 Å, and has occupancy of 12, whereas for a typical oxide such as Ag_2O, the Ag−O shell lies at 2.16 Å, with the first Ag−Ag shell at 3.04 Å.

Purely on the basis of a simple shell model, this erionite sample would therefore appear to contain small silver clusters weakly bonded to the oxygen atoms of the surrounding cage. Five possible models for an Ag_8 cluster were considered in terms of their predicted EXAFS patterns. These included the four SCF optimised structures proposed by Bonačić-Koutecký *et al.* [10], together with a simple cube, and for each of these cluster geometries the expected Ag

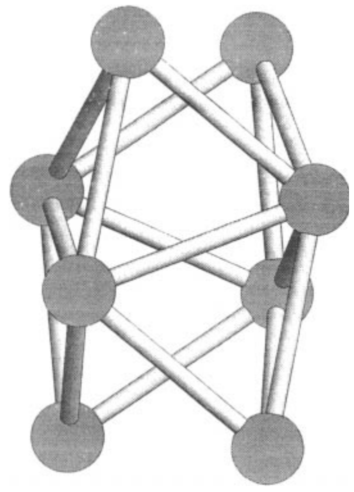

Fig. 2. Minimum energy structure for the cluster Ag_8.

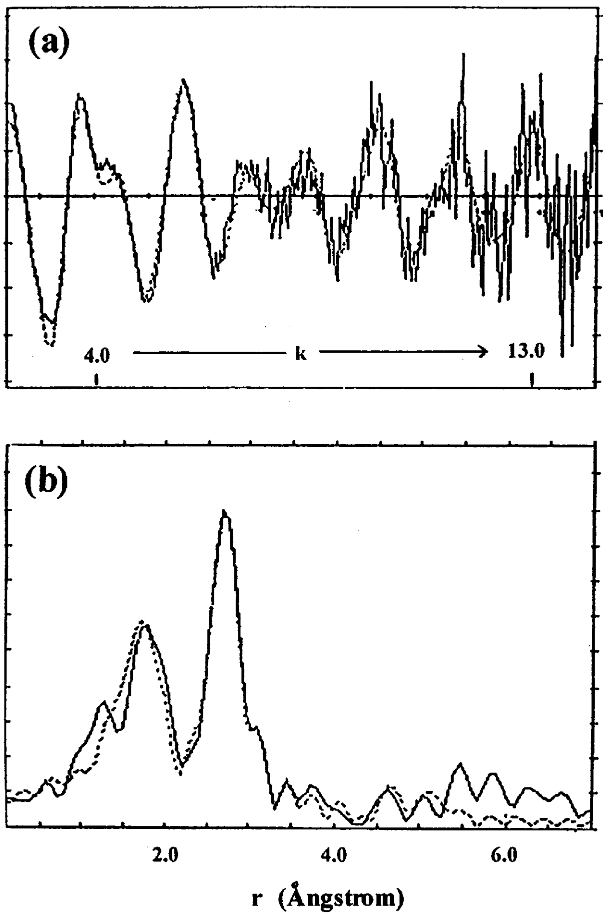

Fig. 3. Observed and calculated EXAFS data for Ag_8 cluster in erionite: (a) EXAFS oscillations; (b) Fourier transforms (solid lines – experimental curves, dotted lines – theoretical curves assuming structure shown in Fig. 2).

EXAFS was calculated and compared with the experimental data. Remarkably, the minimum energy structure predicted from calculation was also the structure that best fitted the EXAFS data, after taking into account a single Ag–O shell. This minimum energy D_{2d} structure is shown in Fig. 2.

A further refinement involving small variations in atom positions, which retained the same overall symmetry, was then carried out, and Fig. 3 compares the observed and calculated EXAFS and Fourier transform data obtained. The R-factor at this stage is 42% for data collected out to $k = 14\,\text{Å}^{-1}$.

These results therefore firstly support the claim that the absorption peaks at 320 nm in the UV spectral region belong to a silver cluster species, in which the Ag–Ag distances are significantly smaller than for the bulk metal. Furthermore, the derived Ag–O distance and shell occupancy are consistent with a uniform surrounding of the silver cluster by oxygen atoms. This indicates that the clusters lie not on the surface, but rather in the channels of the zeolite framework.

The silver content in Ag-erionite is 14 wt. %, that is ~ 20 times as much as in Ag-mordenite (0.66 wt. %). Hence, use of the alkali metal form of erionite resulted in enhancement of silver concentration compared with the protonated form of mordenite. The obtained EXAFS data for Ag-erionite indicate an absence of bulk silver metal and silver oxides. Consequently, silver cluster concentration is close to 14 wt. %. It means that every second erionite cavity contains a silver cluster. The distance between clusters in erionite is significantly shorter than in mordenite. This gives us a reason for suggesting the two peaks at 447 and 683 nm observed in the visible region of the spectrum of Ag-erionite are due to electron transfer between the clusters themselves. Additional experiments will support this hypothesis.

4 Conclusions

The EXAFS data confirm the suggestion that those silver-zeolite samples, which exhibit the characteristic optical absorption at 322 and 293 nm, contain clusters of the species Ag_8 located within the channels. Further analysis of the EXAFS data indicates that the best fit corresponds to an Ag_8 polyhedral cluster with D_{2d} symmetry, which is also the minimum energy structure predicted by calculation.

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