NW10A/2008G687

An XAFS study on Ag⁺ hydration in confinement in nanometer scale

Kanae ITO, Shigeru ISHIDA, Koji YOSHIDA, Toshio YAMAGUCHI* Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

Introduction

The structure and properties of aqueous electrolyte solutions confined in pores in nanometer scale will differ from those in bulk due to both confinement and interaction with the pore wall as in the case of confined water [1]. With recent advances in nanotechnology, chemical processes in the nanoscale have become increasingly important where aqua ions play an important role in preparing nano materials, such as monometallic and bimetallic nanowires [2]. In this study, we examine the effect of confinement on the structure of Ag^+ hydration in a 1.5 M AgNO₃ aqueous solution in confined geometry by XAFS.

Experimental

Porous materials employed were MCM-41 C10 (pore diameter 21 Å) provided by Prof. S. Kittaka (Okayama Univ. Sci.) and Sephadex G-15 (81 Å, Amersham Biosciences). A 1.5 M (M = mol dm⁻³) AgNO₃ aqueous solution was prepared and introduced into the corresponding porous materials with VORTEX MIXER. Inclusion of the sample solutions in the pores were confirmed by DSC measurements. The Ag *K*-edge XAFS spectra were measured over a temperature range of 298 – 190 K with a cryostat at AR-NW10A of the Photon Factory, KEK. The EXAFS spectra were analyzed with program ATHENA.

Results and Discussion

Figure 1 shows the Ag K-edge Fourier Transforms not corrected for the phase shift of a 1.5 M AgNO₃ aqueous solution confined in capillary condensed state in MCM-41 C10 as a function of temperature together with those in Sephadex G15 and in bulk at room temperature. The first predominant peak at 1.7 Å corresponds to the Ag⁺-H₂O bonds within the aqua Ag⁺ ions [3]. For Sephadex G-15 sample, another peak is observed at 2.7 Å, which can be assigned to the Ag-Ag interactions within metallic silver [3]. It appears that a similar peak is also evolved together with a peak at 1.2 Å for MCM-41 sample when the temperature is lowered. Figure 2 shows the Ag K-edge Fourier Transforms of a 1.5 M AgNO₃ aqueous solution confined in monolayer state in MCM-41 C10 as a function of temperature. The spectral pattern of the monolayered sample seems to be similar to that for the capillary condensed state. Apparently, the peak at 1.7 Å becomes sharper with lowering temperature. Interestingly, at 190 K a sharp peak appears at 1.2 Å. A detailed analysis is in progress.



Fig.1. Ag *K-edge* Fourier Transforms of a 1.5 M AgNO₃ aqueous solution confined in capillary condensed state in MCM-41 C10 as a function of temperature.



Fig.2. Ag *K*-edge Fourier Transforms of a 1.5 M AgNO₃ aqueous solution confined in monolayer state in MCM-41 C10 as a function of temperature.

References

[1] P. Smirnov, et al., J. Phys. Chem. 104, 5498 (1998).

[2] M. Ichikawa et al., J. Am. Chem. Soc. 123, 3373 (2001).

[3] T. Yamaguchi et al., Acta Chem. Scand. A38, 423 (1984).

* yamaguch@fukuoka-u.ac.jp