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## Ag K- and L<sub>3</sub>-edge XAFS study on Ag species in Ag/Ga<sub>2</sub>O<sub>3</sub> photocatalysts

M Yamamoto<sup>1</sup>, T Yoshida<sup>2,3</sup>, N Yamamoto<sup>1</sup>, T Nomoto<sup>4</sup>, A Yamamoto<sup>5,6</sup>, H Yoshida<sup>5,6</sup> and S Yagi<sup>3</sup>

<sup>1</sup> Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>2</sup> Advanced Research Institute for Natural Science and Technology, Osaka City University, Osaka 558-8585, Japan

<sup>3</sup> EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan

<sup>4</sup> Aichi Synchrotron Radiation Center, Seto 489-0965, Japan

<sup>5</sup> Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

<sup>6</sup> Element Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan

E-mail: yamamoto.muneaki@f.mbox.nagoya-u.ac.jp, tyoshida@ocarina.osaka-cu.ac.jp

**Abstract.** Ag loaded Ga<sub>2</sub>O<sub>3</sub> (Ag/Ga<sub>2</sub>O<sub>3</sub>) shows photocatalytic activity for reduction of CO<sub>2</sub> with water. Ag L<sub>3</sub>-edge XANES and K-edge EXAFS spectra were measured for various Ag/Ga<sub>2</sub>O<sub>3</sub> samples, which suggested that structural and chemical states of Ag species varied with the loading amount of Ag and the preparation method. The Ag species were metallic Ag particles with an AgGaO<sub>2</sub>-like interface structure in the sample with high loading amount of Ag while predominantly Ag metal clusters in the sample with low loading amount of Ag. The XANES feature just above the edge represented the interaction between the Ag species and the Ga<sub>2</sub>O<sub>3</sub> surface, showing that the Ag metal clusters had more electrons in the *d*-orbitals by interacting with the Ga<sub>2</sub>O<sub>3</sub> surface, which would contribute the high photocatalytic activity.

### 1. Introduction

An increasing concentration of atmospheric CO<sub>2</sub> has become a concern for our planet. One of the solutions for this problem, photocatalytic reduction of CO<sub>2</sub> to other useful chemicals has attracted much attention [1–4]. For the CO<sub>2</sub> reduction, an external energy and an appropriate catalyst are required, since CO<sub>2</sub> is one of the most stable molecules. Recently, it has been reported that Ag loaded Ga<sub>2</sub>O<sub>3</sub> (Ag/Ga<sub>2</sub>O<sub>3</sub>) shows the photocatalytic activity for reduction of CO<sub>2</sub> with water to produce CO [5–7]. In our previous study [8], we found that the chemical state of Ag species in as-prepared Ag/Ga<sub>2</sub>O<sub>3</sub> samples affected the formation process of the reaction intermediate, which were closely related to the CO production efficiency. However, it is still unclear how the structural and chemical states of the Ag species as well as Ag–Ga<sub>2</sub>O<sub>3</sub> interaction change with the loading amount of Ag. In the present study, Ag L<sub>3</sub>-edge and K-edge XAFS analysis was applied to investigate the structural and chemical states of the Ag species, which provided us meaningful information for understanding the photocatalysis of Ag/Ga<sub>2</sub>O<sub>3</sub> samples.



## 2. Experimental

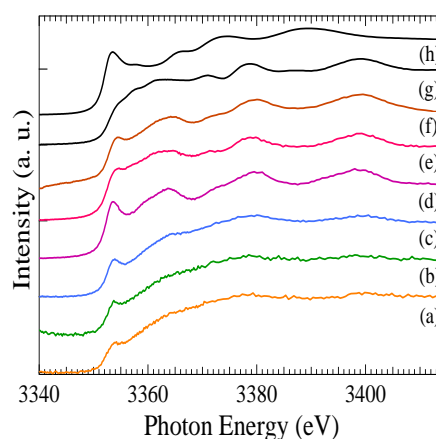
Ag/Ga<sub>2</sub>O<sub>3</sub> samples were prepared by an impregnation (IMP) method and a photodeposition (PD) method. Generally, it is expected that IMP method provides Ag ions well interacting with the Ga<sub>2</sub>O<sub>3</sub> support while PD method is suited to the formation of metallic Ag species. For IMP method, a mixture of Ga<sub>2</sub>O<sub>3</sub> powders and an aqueous solution of AgNO<sub>3</sub> was magnetically stirred and dried, followed by calcination at 673 K for 2 h. The loading amounts of Ag were 0.1, 0.2, 0.5, 1.0 and 5.0 wt%. For PD method, a mixture of a Ga<sub>2</sub>O<sub>3</sub> powder and an aqueous solution of AgNO<sub>3</sub> with ethanol was magnetically stirred and photoirradiated for 3 h, followed by filtration. The loading amounts of Ag were 0.1 and 1.0 wt%. Ag L<sub>3</sub>-edge XAFS measurements were carried out in a fluorescent X-ray yield mode and in a total electron yield mode at the beam line 6N1 at the Aichi Synchrotron Radiation Center (Proposal No. 2503042). Ag K-edge XAFS spectra were measured at the NW10A station at the Photon Factory in the fluorescence mode with a 19 element solid state Ge detector and in a transmission mode (Proposal No. 2014G547).

## 3. Results and discussion

In our previous study [8], TEM and HAADF-STEM measurements revealed that around 1 nm sized Ag clusters were formed predominantly in a 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) photocatalytic active sample while Ag particles with the size of several–several tens nm in a 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample. In a 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample and a 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD) sample, large Ag particles with the size of over 30 nm were observed. After heating the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD) sample at 673 K for 2 h, the average Ag particle size became smaller as 1–2 nm and they were highly dispersed on the Ga<sub>2</sub>O<sub>3</sub> surface.

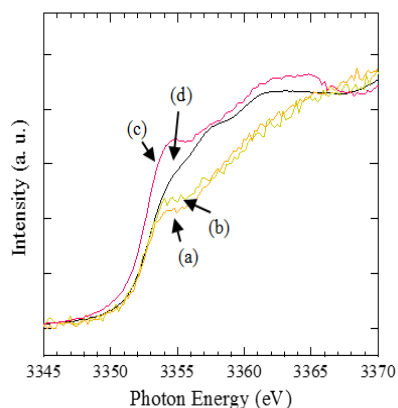
In the present study, the Ag species in the Ag/Ga<sub>2</sub>O<sub>3</sub> samples were investigated in detail by Ag L<sub>3</sub>- and K-edge XAFS spectroscopy. Figure 1 shows the spectra of the Ag/Ga<sub>2</sub>O<sub>3</sub> samples together with Ag foil and Ag<sub>2</sub>O as references. We tried to simulate the XANES spectra of the Ag/Ga<sub>2</sub>O<sub>3</sub> samples by using the reference spectra, but the fitting was not sufficient, indicating that the Ag species in the Ag/Ga<sub>2</sub>O<sub>3</sub> samples were not a simple mixture of metal and oxides. As is evident from figure 1, the XANES spectrum of the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample has no distinct peaks, which originates from highly dispersed Ag species such as 1 nm sized Ag clusters [8]. With increasing the loading amount of Ag, the feature of XANES changed gradually to the characteristic one of an Ag bulk.

Note that the peak at 3353 eV grew with the loading amount of Ag up to 1.0 wt%, and then decreased with 5.0 wt% loading. This peak has been assigned to the transition from 2p to unoccupied 4d states [9]. The peak was clearly shown in the spectrum of Ag<sub>2</sub>O. Therefore, in the Ag/Ga<sub>2</sub>O<sub>3</sub> samples with higher loading amount of Ag up to 1.0 wt%, most of Ag species would be partially oxidized. As for the 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>, XANES spectra could be measured both in a fluorescent X-ray yield mode (FY) and a surface sensitive total electron yield mode (TEY) as shown in figures 1e and 1f. The former spectrum (FY) was similar to that of an Ag bulk, suggesting that Ag species was metallic. Nevertheless, a small peak at 3353 eV evidenced the existence of oxides. In the latter spectrum (TEY), this peak was clearly seen and more thorough observation suggested that double peaks at 3364 and 3380 eV became intense, which were similar to the characteristic feature of 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub>. This result indicates that the Ag species in the 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> sample is almost metallic Ag like an Ag bulk, but the surface is slightly oxidized. In addition, it is also suggested that the Ag species in 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> would be partially oxidized Ag particles or a mixture of the metallic and oxidized species, which will be discussed below.

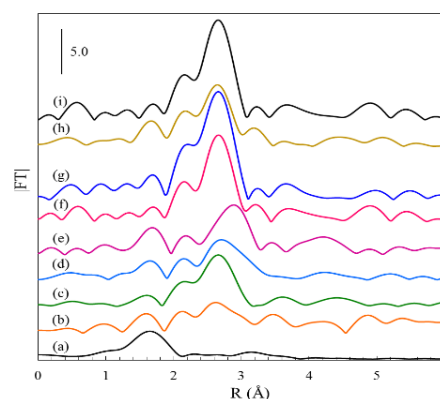


**Figure 1.** Ag L<sub>3</sub>-edge XANES spectra of the Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples (a–f), Ag foil (g) and Ag<sub>2</sub>O (h). Ag loading (wt%): 0.1 (a), 0.2 (b), 0.5 (c), 1.0 (d), 5.0 (FY) (e) and 5.0 (TEY) (f).

Figure S1 in the supporting information shows the Ag L<sub>3</sub>-edge XANES spectra of the 0.1 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD) samples. Since both the spectra were very similar to that of an Ag bulk, the Ag species in the 0.1 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD) samples were metallic Ag. It was also confirmed that the broad feature shown in the XANES of the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample was not due to



**Figure 2.** Ag L<sub>3</sub>-edge XANES spectra of the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample (a), the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) sample (b), the 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample (c) and Ag foil (d).



**Figure 3.** Radial structure functions of Ag<sub>2</sub>O (a), the Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples (b–f), the Ag/Ga<sub>2</sub>O<sub>3</sub> (PD, PD-H) samples (g, h) and Ag foil (i). Ag loading (wt%): 0.1 (b), 0.2 (c), 0.5 (d), 1.0 (e), 5.0 (f), 1.0 (g) and 1.0 (h).

the low loading amount of Ag. Figure S1, c–f shows the Ag L<sub>3</sub>-edge XANES spectra of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> samples prepared by the PD method, followed by heating in air for 2 h at various temperatures, referred to as Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H). A small shoulder around 3353 eV would indicate some oxidized moiety in the samples. With increasing the heating temperature, the XANES feature became broad gradually and at more than 573 K, the spectra were similar to that of the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample. Considering the TEM results in our previous study [8], the spectral change is assignable to the decrease of the Ag particle size by heating at more than 573 K. The decrease of the particle size suggests the strong interaction between the Ag particle and the Ga<sub>2</sub>O<sub>3</sub> surface.

In Figure 2, the characteristic XANES feature just above the edge would represent the interaction between the Ag species and the Ga<sub>2</sub>O<sub>3</sub> surface. The Ag/Ga<sub>2</sub>O<sub>3</sub> samples showed lower absorption around 3350–3365 eV than that of an Ag bulk. This feature was most significant for the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample and the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> heated at 623 K (PD-H) sample. Similar features around 3350–3365 eV were reported for Au–Ag alloys and Ag clusters on Au rods by some researchers [10–12]. They concluded that the electron density in the *d*-orbital of the Ag atom increased by transferring electrons from Au to Ag. Therefore, in the present 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample and the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) sample, the Ag species would probably accept more electrons in the *d*-orbitals from the Ga<sub>2</sub>O<sub>3</sub> surface as the result of the strong interaction.

Figure 3 shows radial structure functions (RSF) obtained by Fourier transform of *k*<sup>3</sup>-weighted Ag K-edge EXAFS (Figure S2 in supporting information) in the region of *k* = 3.15–11.80 Å<sup>-1</sup>. The small peak around 1.7 Å was assigned to the Ag–O pair and/or side lobes, and this peak was larger for the 0.5 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP), the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) and the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) samples. The peak around 2.5–3 Å observed for all the Ag/Ga<sub>2</sub>O<sub>3</sub> samples should correspond to the Ag–Ag pair. As for the Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples, this peak grew with the loading amount of Ag, although it became broader and shifted to longer *R* region for the 0.5 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples.

We also performed curve-fitting analysis on the back Fourier-transformed EXAFS from the first and the second coordination shells (*R* = 1.35–3.35 Å) as summarized in Table S1 in supporting information. The average Ag–Ag distance was estimated to be ca. 2.89 Å for the 0.1, 0.2 and 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples, which was in good agreement with that of the Ag foil. Note that the photocatalytically active Ag clusters formed predominately in the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample were metallic. The average coordination number for the Ag–Ag shell (CN<sub>Ag</sub>) for 5.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) was close to that of Ag foil, suggesting the large Ag metal particles, while the CN<sub>Ag</sub> values for the 0.1 and 0.2 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples were 4.3 and 6.5, respectively, which were significantly smaller than that of

the Ag foil. The geometrical calculation for the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) sample demonstrated that the Ag species with the CN<sub>Ag</sub> values of 4.3 would be smaller than 1 nm, such as metallic cluster, which was quite consistent with the HAADF-STEM result of this sample [8].

On the other hand, the 0.5 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples had two types of short (2.89 Å) and long (3.05 Å) Ag–Ag pairs. The latter was longer than that of Ag metal and similar to the Ag–Ag distance (3.03 Å) in AgGaO<sub>2</sub> [13]. The Ag–O pair with 2.10–2.12 Å in length which was longer than those of Ag<sub>2</sub>O and AgO and similar to the Ag–O distance (2.10 Å) in AgGaO<sub>2</sub> [13]. These suggest that a part of Ag atoms at the interface between the Ag metal particle and the Ga<sub>2</sub>O<sub>3</sub> surface would be in an AgGaO<sub>2</sub>-like structure as a result of well interaction with the Ga<sub>2</sub>O<sub>3</sub> surface and other part would form Ag metal particles. In the cases of the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD) and the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) samples, the average Ag–Ag distance was estimated to be 2.89 Å for both samples and CN<sub>Ag</sub> for the former and the latter samples to 11.9 and 7.3, demonstrating that the large Ag metal particles changed to small ones by heating. It is also noteworthy that the Ag–O pair was found only for the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) sample and the 0.5 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples. Since another Ag–Ag pair of long distance was not recognized for the 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (PD-H) sample, this Ag–O bond might be formed by the interaction of small Ag metal particles with Ga<sub>2</sub>O<sub>3</sub> support.

#### 4. Conclusion

We investigated the structural and chemical states of the Ag species as well as its interaction with the Ga<sub>2</sub>O<sub>3</sub> surface by measuring Ag L<sub>3</sub> and K-edge XAFS of the Ag/Ga<sub>2</sub>O<sub>3</sub> samples. There were some kinds of Ag species such as around 1 nm sized Ag metal cluster in the Ag low loading samples and metallic Ag particles in the Ag high loading samples. The AgGaO<sub>2</sub>-like interface structure would be formed between metallic Ag particles and the Ga<sub>2</sub>O<sub>3</sub> surface, observed in the 0.5 and 1.0 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> (IMP) samples. In the 0.1 wt% Ag/Ga<sub>2</sub>O<sub>3</sub> sample that was photocatalytically active sample, the Ag metal clusters with the size of around 1 nm were formed predominantly, and they probably accepted more electrons in the *d*-orbitals by the interaction with the Ga<sub>2</sub>O<sub>3</sub> surface. These differences in structural and chemical states of the Ag species would affect the photocatalytic activity of CO<sub>2</sub> reduction with water.

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