

XAFS analysis of Au species formed on calcium silicide

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1 Introduction

Various techniques enable to use for preparation of noble metal-loaded catalysts. Noble metals play crucial roles as beneficial catalysts in versatile reactions. Chemical reduction method, photo-deposition, microwave irradiation and others are investigated in recent years. Metal oxides are mainly adopted as support materials.

On the other hand, silicide is composed of abundant elements and mainly used in a bulk form or thin films. Some researchers focus on the utilization of calcium silicide (CaSi₂), which is composed of abundant elements and has a unique layered structure of calcium cation and silicon. The electrons are also delocalized in the silicon layer. In our previous work, we report on the successful synthesis of a flower like structured CaSi₂ through a simple treatment of bulk CaSi₂ powder in aqueous NaOH solution [1]. Based on this result, we focus on the synthesis of metal nanoparticles on CaSi₂ as a catalyst support by using unique property of CaSi₂. In the present study, XAFS investigations were carried out to confirm the chemical state of Au species formed on CaSi₂.

2 Experiment

CaSi₂ was purchased from Kojundo chemical lab. co. ltd., and was finely crushed by a planetary ball mill. The treatment of CaSi₂ in an aqueous HAuCl₄ solution was carried out by following process. After CaSi₂ was suspended in an aqueous HAuCl₄ solution in a flask and shook at 298 K for 1 h, sample was recovered by centrifugation, dried under vacuum at 298 K after washing by deionized water.

XAFS spectra at Au L₃-edge were measured in the transmission mode for reference samples and fluorescence mode for target sample at 298 K. Samples were sealed within polyethylene film under an argon atmosphere. Obtained data were examined using the analysis program (Rigaku REX2000).

3 Results and Discussion

Although the color change of the solution was hardly observed by the addition of SiO₂ in an aqueous HAuCl₄ solution, the disappearance was clearly observed in the case of CaSi₂. The color of the solution gradually disappeared corresponding to the mixing time. It was also confirmed that the amount of Au species charged (1.0 wt % as metal) were completely fixed on CaSi₂ even after washing by deionized water. To confirm the state of Au species on CaSi₂, XAFS measurement was carried out at

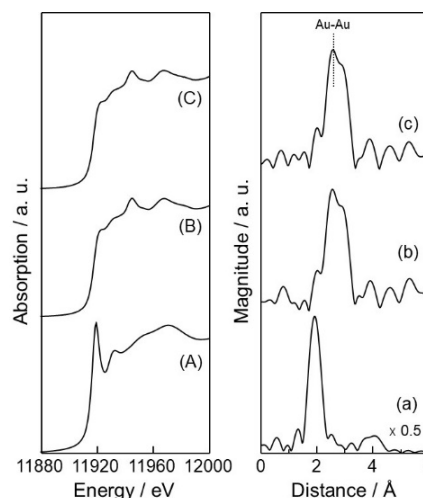


Figure 1. (A-C) XANES and (a-c) Fourier transforms of the EXAFS spectra of (A,a) aqueous HAuCl₄ solution, (B,b) Au foil, and (C, c) CaSi₂ after treatment in an aqueous HAuCl₄ solution, respectively.

Au L₃-edge. As shown in Fig. 1, the shape and the edge position of X-ray absorption near-edge structure (XANES) spectrum of CaSi₂ after treatment in an aqueous HAuCl₄ solution was similar to that of Au foil as a reference, showing that the metallic Au was formed on CaSi₂ by only mixing in an aqueous HAuCl₄ solution. In Fourier transforms of the EXAFS spectrum, typical peak due to the presence of the Au-Au bond of the metallic Au was observed at around 2.5 Å (without phase-shift correction). These results indicated the formation of Au metal on CaSi₂ through the reduction of Au ion without the addition of a reducing agents such as NaBH₄ and others. CaSi₂ has a potential for loading of Au metal through the unique reduction process of Au ion to metal.

The formation of small and highly dispersed Au nanoparticles with a narrow size distribution was also confirmed by TEM measurement. This sample was also worked as a heterogeneous catalyst with a high catalytic performance in the reduction of 4-nitrophenol to 4-aminophenol.

References

- [1] T. Kamegawa *et al.*, *Bull. Chem. Soc. Jpn.*, **94**, 2089 (2021).

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