AR-NW10A/2013S2-002

$12CaO{\cdot}7Al_2O_3$ Electride Gives High Oxidation Tolerance to Ru Nanoparticles

Hitoshi Abe[1,2,3,*] and , Yasuhiro Niwa[1], Masaaki Kitano[4], Yasunori Inoue[5], Youichi Murakami[1,2], Toshiharu Yokoyama[3,4], Michikazu Hara[3,5,6], and Hideo Hosono[3,4,5,6]

[1]Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, 305-0801, Japan

[2]School of High Energy Accelerator Science, SOKENDAI, 1-1 Oho, Tsukuba, 305-0801, Japan

[3]ACCEL, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, 332-0012, Japan

[4]Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

[5]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

[6]Frontier Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

1 Introduction

Electrides are a class of compounds where electrons behave as anions [1,2]. The first inorganic electride, $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (C12A7:e^-) was produced by Matsuishi, *et al.* [3]. The C12A7:e^- having a chemical stability and a low work function could work as an electron donor. An efficient ammonia synthesis using Ru/C12A7:e^- has been reported [4], and the high catalytic activity is explained by strong electron donating ability of C12A7:e^-.

We report the high tolerance to oxidation of Ru nanoparticles on C12A7:e^- observed by *in situ* XAFS measurements [5].

2 Experiment

XAFS measurements were performed at AR-NW10A. 2wt% Ru/C12A7:e^- was measured by transmission mode using an *in situ* cell with gas flow controlled. As a reference, 6wt% Ru/Al_2O_3 was also measured.

Oxidation processes were carried out under flow of O_2 45 cm^3 min^{-1} balanced with He 15 cm^3 min^{-1} with increasing temperature up to 773 K at a rate of 5 K min^{-1}.

3 Results and Discussion

Ru *K*-edge XANES spectra obtained during the oxidation process are shown in Fig. 1. As shown in Fig. 1(a), 6wt% Ru/Al_2O_3 was rapidly oxidized just after switching to the oxidation condition at room temperature. Then, it was gradually oxidized to be the state of RuO_2.

Ru *K*-edge XANES spectra of 2wt% Ru/C12A7:e^- obtained during the oxidation condition are shown in Fig. 1(b). The edge shifted to a little higher energy by increasing temperature, but the shift was smaller 3 eV at largest. The spectra recorded at 773 K was still close to that of Ru metal rather than RuO_2.

The Ru nanoparticles of 2wt% Ru/C12A7:e^- at 773 K stayed mostly metallic although they were under the strong oxidation condition at the elevated temperature. We can conclude that they have a high tolerance to oxidation even in the form of nanoparticles.

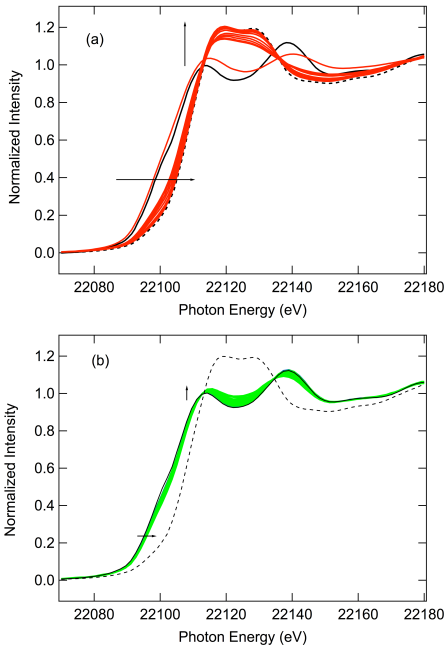

Fig. 1: Ru *K*-edge XANES spectra obtained during the oxidation condition, (a) 6wt% Ru/Al_2O_3 (red) and (b) 2wt% Ru/C12A7:e^- (green), together with Ru metal (solid) and RuO_2 (dashed).

Acknowledgement

This work was supported by a fund from Accelerated Innovation Research Initiative Turning Top Science and Ideas into High-Impact Values (ACCEL) of Japan Science and Technology Agency. A part of this research was supported by MEXT Element Strategy Initiative to form a research core.

References

[1] J. Dye, *Science* **247**, 663 (1990).
[2] J. Dye, *Science* **301**, 607 (2003).
[3] S. Matsuishi, et al., *Science* **301**, 626 (2003).
[4] M. Kitano, *et al.*, *Nat. Chem.* **4**, 934 (2012).
[5] H. Abe, *et al.*, *J. Phys. Chem. C* **120**, 8711 (2016).

* hitoshi.abe@kek.jp