12CaO-7Al₂O₃ Electride Gives High Oxidation Tolerance to Ru Nanoparticles

Hitoshi Abe¹,²,³*, Yasuhiro Niwa¹, Masaaki Kitano⁴, Yasunori Inoue⁵, Youichi Murakami¹,², Toshiharu Yokoyama¹,⁴, Michikazu Hara³,⁵,⁶, and Hideo Hosono³,⁴,⁵,⁶

¹Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, 305-0801, Japan
²School of High Energy Accelerator Science, SOKENDAI, 1-1 Oho, Tsukuba, 305-0801, Japan
³ACCEL, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, 332-0012, Japan
⁴Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
⁵Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
⁶Frontier 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 electrode, [Ca₂₆Al₂O₈]⁺⁺⁻(e)₄⁺ (C₁₂₂₇:⁺) was produced by Matsuishi, et al. [3]. The C₁₂₂₇:⁺ having a chemical stability and a low work function could work as an electron donor. An efficient ammonia synthesis using Ru/C₁₂₂₇:⁺ has been reported [4], and the high catalytic activity is explained by strong electron donating ability of C₁₂₂₇:⁺.

We report the high tolerance to oxidation of Ru nanoparticles on C₁₂₂₇:⁺ observed by in situ XAFS measurements [5].

2 Experiment

XAFS measurements were performed at AR-NW10A, 2wt% Ru/C₁₂₂₇:⁺ was measured by transmission mode using an in situ cell with gas flow controlled. As a reference, 6wt% Ru/Al₂O₃ was also measured.

Oxidation processes were carried out under flow of O₂ 45 cm³ min⁻¹ balanced with He 15 cm³ 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/Al₂O₃ was rapidly oxidized just after switching to the oxidation condition at room temperature. Then, it was gradually oxidized to be the state of RuO₂.

Ru K-edge XANES spectra of 2wt% Ru/C₁₂₂₇:⁺ 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 RuO₂.

The Ru nanoparticles of 2wt% Ru/C₁₂₂₇:⁺ 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/Al₂O₃ (red) and (b) 2wt% Ru/C₁₂₂₇:⁺ (green), together with Ru metal (solid) and RuO₂ (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
* hitoshi.abe@kek.jp