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Demonstration of In Situ High-Pressure Photocatalytic Cell for XAFS Measurements

Masaya Miyano,[1] Hongwei Zhang,[1] and Yasuo Izumi[1,*]

[1] *Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan*

1 Introduction

Charge transfer is a key step in photocatalysis and more efficient charge transfer from surface to substrates is expected if the pressure of reactants is elevated. We recently demonstrated promoted photocatalytic CO_2 conversion into fuels (methane, methanol, and CO) at 0.40–0.80 MPa using several semiconductor-based photocatalysts including layered double hydroxides (LDHs) [1,2].

However, complex dependence of photocatalytic rates on reactant pressure, i.e. $P(CO_2)$ and $P(H_2)$, was observed when H_2 was used as a reductant instead of H_2O, resulting in volcano-type dependence peaked at $P(CO_2) = 0.12$ kPa and $P(H_2) = 0.28$ kPa [3]. Hence, the states of the active sites in LDH photocatalyst were investigated by in situ XAFS at high pressure in this study.

2 Experimental Section

Zn and Ga K-edge XAFS spectra were measured in the KEK Photon Factory on beamline 12C. The storage ring energy was 2.5 eV. A Si (1 1 1) double-crystal monochromator and a pair of bent cylindrical mirrors were inserted into the X-ray beam path.

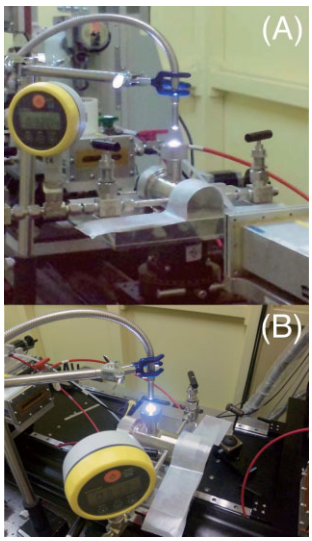

Fig. 1: Homemade high-pressure photocatalytic reactor for in situ XAFS measurements. **(A)** Side view and **(B)** top view.

The $[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ LDH sample was set in a homemade stainless reactor equipped with a pressure gauge, diamond windows (thickness 0.50 mm) for X-ray and a quartz window (thickness 4.0 mm) for UV–visible light (Fig. 1). 0.18 kPa of CO_2 and 0.42 kPa of H_2 were introduced to the reactor and the LDH sample was irradiated by UV–visible light provided by a 500-W xenon arc lamp (Ushio). XAFS data were analyzed using the XDAP software package.

3 Results and Discussion

The Zn K-edge and Ga K-edge XANES spectra during CO_2 photoconversion test at 0.60 MPa are shown in Fig. 2A and B, respectively. Under the condition, CO_2 is photoconverted into methane and methanol [1]. Corresponding to the performance, the whiteline peak intensity at 10379 eV near the Ga K-edge decreased by 2.1% when the UV–visible light was irradiated as compared to that under dark. In contrast, the whiteline peak intensity at 9671 eV near the Zn K-edge negligibly changed or decreased only by 1.2% when the UV–visible light was irradated as compared to that under dark. This change of whiteline peak intensity by the UV–visible light irradiation was only observed at elevated pressure, and not at 0.1 MPa.

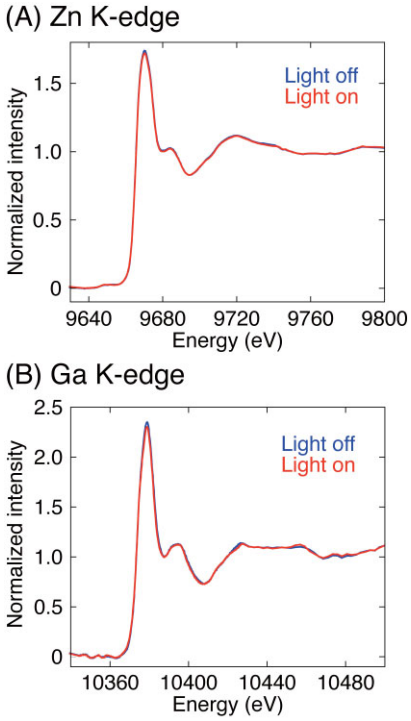

Fig. 2: In situ XANES spectra at **(A)** Zn K-edge and **(B)** Ga K-edge for $[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ LDH under CO_2 (0.18 MPa) and H_2 (0.42 MPa) and UV–visible light irradiation at beamline (Fig. 1).

The decrease of whiteline intensity should be related to the partial occupancy of 4s and 4p states by the

photogenerated electrons. The possibility of partially reduced Ga ions adsorbed with intermediate species at elevated pressure needs to be verified.

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* yizumi@faculty.chiba-u.jp