12C, NW10A/2016G577

Monitoring of Electron Diffusion During High-Pressure CO_2 Photoconversion in Layered Double Hydroxides

Hongwei Zhang,[1] Lukas Anton Wein,[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

Charges are spacially separated when semiconductors are irradiated by ultraviolet (UV) or visible light whose light energy is higher than the band gap of semiconductors. It is quite advantageous to reduce CO_2 into fuels using the separated electrons in semiconductors in viewpoint of global warming and energy shortage [1]. We recently reported promoted CO_2 photoconversion into methanol using layered double hydroxides (LDHs) preheated at 423 K. The optimum reaction pressure was 0.40 MPa, i.e. 0.12 MPa of CO_2 and 0.28 MPa of H_2 [2]. In this report, electron diffusion created by UV–visible light to the surface Cu active sites in/on LDHs for CO_2 conversion was monitored by in situ X-ray absorption near-edge structure (XANES).

2 Experimental Section

Zn, Cu, and Ga K-edge XAFS spectra were measured in the KEK Photon Factory on beamline 12C and Photon Factory Advanced Ring on beamline NW10A.

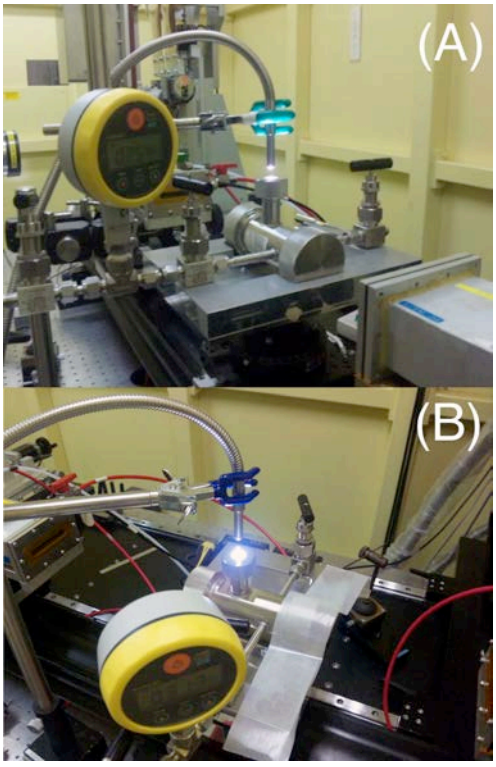

Fig. 1 Homemade high-pressure photocatalytic reactor for in situ XAFS measurements. **(A)** Side view and **(B)** top view.

$[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ (abbreviated as Zn–Ga–CO_3) and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2CO_3{\cdot}mH_2O$ (abbreviated as Zn–Cu-Ga–CO_3) LDHs were synthesized as described in Ref. 2. The disk samples were 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). 0.12–0.18 MPa of CO_2 and 0.28–0.42 MPa of H_2 were introduced to the reactor and the LDH sample was irradiated by UV–visible light provided by a 500-W Xe arc lamp (Ushio, model SX-UID502XAM). Obtained XANES data were analyzed using the XDAP software package.

3 Results and Discussion

In-situ Cu K-edge XANES of the most active Zn–Cu–Ga–CO_3 [2] was monitored under reactant pressures of 0.12 MPa CO_2 and 0.28 MPa H_2 irradiated by UV–visible light during measurement at beamline for 2 h (Fig. 1). The 1s-3d preedge peak appeared at 8980.6 eV (Fig. 2A, inset). The peak intensity progressively decreased (Fig. 2B) due to the reduction of Cu(II) ($3d^9$ configuration) to Cu(I) ($3d^{10}$ configuration) by the diffusion of photogenerated electrons to the Cu sites. 1s-3d electronic transition is impossible to fully occupied $3d^{10}$ Cu site. The peak decreasing rate corresponds to 170 μmol-Cu h^{-1} g_{cat}^{-1} for 25 mg-disk sample of Φ = 1.0 cm.

Under 2.1 kPa of CO_2 and 21.7 kPa of H_2, Cu site reduction rate of 580 μmol-Cu h^{-1} g_{cat}^{-1} was reported under similar conditions for 170 mg-disk Zn–Cu–Ga–CO_3 sample of Φ = 2.0 cm [3,4]. The reduction rate of Cu at 0.40 MPa was 10 times greater compared to its methanol formation rate (2.8 μmol-methanol h^{-1} g_{cat}^{-1} [2]), taking the electron number(s) needed for each reaction (Cu(II)/(I) redox *versus* six electron reduction to methanol) into account. Thus, the inlayer Cu sites once accumulate photogenerated and diffused electrons. However, the electrons transfer to CO_2 (or CO_2-derived species) more easily under pressurized conditions (Fig. 2) in comparison to that at a lower pressure (23.8 kPa) [3,4]. Thereby the net Cu reduction rate during this experiment (Figure 2B) seemed to be lower in comparison to that in references 3 and 4.

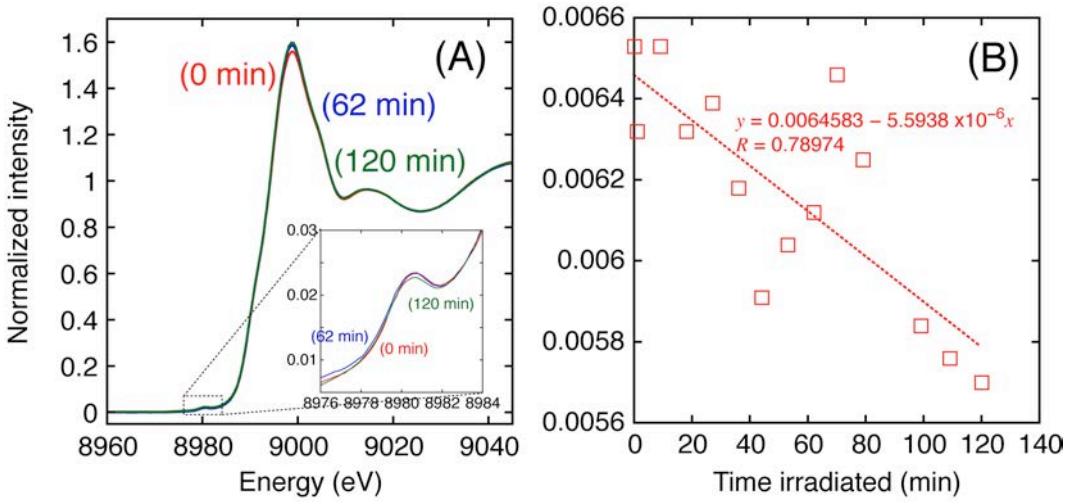

Fig. 2 (A) In situ normalized Cu K-edge XANES spectra for Zn–Cu–Ga–CO_3 (25 mg) under CO_2 (0.12 MPa) and H_2 (0.28 MPa) and UV–visible light irradiation for 0 min, 62 min, and 120 min at beamline. **(Inset)** Expanded view of 1s-3d preedge peak region. **(B)** Time course of the intensity of 1s-3d preedge peak for 2 h.

Acknowledgements

The authors are grateful for the financial supports from the Grant-in-Aid for Scientific Research C (17K05961, 26410204) from Japan Society for the Promotion of Science and Leading Research Promotion Program (2015–) from the Institute for Global Prominent Research, Chiba University. X-ray absorption experiments were conducted under the approval of the Photon Factory Proposal Review Committee.

References

[1] Y. Izumi, *Coord. Chem. Rev.* **257**, 171–186 (2013).
[2] L. A. Wein, H. Zhang, K. Urushidate, M. Miyano, and Y. Izumi, *Appl. Surf. Sci.* **447**, 687–696 (2018).
[3] M. Morikawa, N. Ahmed, Y. Yoshida, Y. Izumi, *Appl. Catal. B* **144**, 561–569 (2014).
[4] Y. Izumi, S. Kawamura, M. Morikawa, A. Naveed, *Photon Factory Act. Rep.* **31**(Highlights), 36–37 (2014).

Research Achievements

Related work to this study monitoring electrons in semiconductuctor photocatalysts for CO_2 photoconversion is reported as Highlights in *Photon Factory Activity Report 2017*.

* yizumi@faculty.chiba-u.jp