

## Partial Reduction of Copper/Cerium Oxide Catalyst to Activate Carbon Dioxide to Form Dimethyl Carbonate Monitored by Ce L<sub>3</sub>-edge XAFS

Seiki Wada<sup>1</sup> and Yasuo Izumi\*<sup>1</sup>

<sup>1</sup>Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

### Introduction

The importance of catalytic conversion of CO<sub>2</sub> into harmless, useful compounds is recognized again in relation to environmental problem. We recently reported photocatalytic conversion of CO<sub>2</sub> into methanol [1]. If the unreacted CO<sub>2</sub> is catalytically coupled with produced methanol to form dimethyl carbonate (DMC), CO<sub>2</sub> is fixed as harmless, useful compound applied as an electrolytic solution of lithium ion rechargeable battery.

In this work, new catalyst to synthesize DMC from CO<sub>2</sub> and methanol was investigated in mild reaction condition, *e.g.* 373 K and 1 MPa. The best catalyst was Cu/CeO<sub>2-x</sub> pre-reduced at 673 K. The reason why this catalyst worked well was investigated by using Ce L<sub>3</sub>-edge XAFS.

### Methods

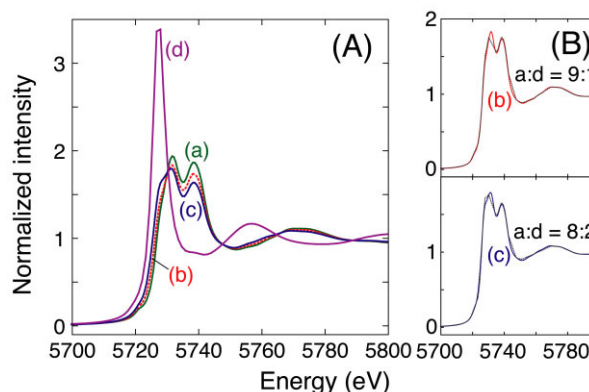
CeO<sub>2</sub> was synthesized by the addition of ammonia to Ce<sup>III</sup> nitrate solution. To the light yellow powder obtained after the calcination at 673 K, copper nitrate solution was added and the pH was controlled at 9.5. The obtained powder was heated at 673 K in hydrogen for 1 h. Thus-prepared catalyst sample for the batch reaction test of CO<sub>2</sub> and methanol in an autoclave was transferred to the airtight Pyrex glass cell and transported to beamline. Ce L<sub>3</sub>-edge XAFS spectra were measured at 290 K at beamline 7C, 9A, or 9C in transmission mode.

### Results and Discussion

CeO<sub>2</sub> produced DMC with the rate of 0.44 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> at 393 K and 3.5 MPa (CO<sub>2</sub> 2.9 MPa; methanol 0.64 MPa). The rate was improved to 0.70 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> in the same reaction condition over CeO<sub>2</sub> pre-reduced at 673 K in H<sub>2</sub>.

In a milder reaction condition at 393 K and 1.3 MPa (CO<sub>2</sub> 0.67 MPa; methanol 0.64 MPa), DMC formation rate was 0.41 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> using pre-reduced CeO<sub>2-x</sub>. The rate was further increased using Cu/CeO<sub>2</sub> consisting of 0.1 wt% of Cu pre-reduced at 673 K in H<sub>2</sub> (0.95 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>).

The Ce L<sub>3</sub>-edge XANES spectra for CeO<sub>2</sub>-based catalysts and a reference are depicted in Figure 1A. Typical twin peaks appeared at 5731.9 and 5738.7 eV for as-synthesized CeO<sub>2</sub> (a) and the pattern was



**Figure 1.** (A) Ce L<sub>3</sub>-edge XANES for as-synthesized CeO<sub>2</sub> (a), CeO<sub>2</sub> reduced at 673 K (b), Cu/CeO<sub>2</sub> (0.1 wt% Cu) reduced at 673 K (c), and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (d). (B) Fits to spectra b and c with the combination of spectra a and d. Best fit results were shown by changing the mixing ratio of data a and d.

similar to that for (NH<sub>4</sub>)<sub>2</sub>Ce<sup>IV</sup>(NO<sub>3</sub>)<sub>6</sub> (the spectrum not shown), indicating the contribution of Ce<sup>IV</sup>. In contrast, single, more intense peak appeared at 5727.4 eV for Ce<sup>III</sup>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (d).

Then, spectra b and c for pre-reduced CeO<sub>2-x</sub> and pre-reduced Cu/CeO<sub>2-x</sub> were fit with the combination of data for as-synthesized Ce<sup>IV</sup>O<sub>2</sub> and Ce<sup>III</sup>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O by changing the mixing ratio. The spectrum b was best fit when the mixing ratio was 9:1 while the spectrum c was best fit with the mixing ratio 8:2 (Figure 1B). Hence, the population of Ce<sup>III</sup> sites was 10% upon reduction of CeO<sub>2</sub> at 673 K and the reduction to Ce<sup>III</sup> was promoted further to 20% with the doped Cu.

The catalytic DMC formation rates increased linearly as the partial pressure of CO<sub>2</sub> increased (0.13–2.9 MPa) for pre-reduced Cu/CeO<sub>2-x</sub> catalyst. Reduced Ce<sup>III</sup> sites were suggested to adsorb CO<sub>2</sub> and the probability of nucleophilic attack of methoxy on the carbon of CO<sub>2</sub> increased.

### References

[1] N. Ahmed, Y. Shibata, T. Taniguchi, Y. Izumi, *J. Catal.* **279**(1), 123–135 (2011).

\* yizumi@faculty.chiba-u.jp