Partial Reduction of Copper/Cerium Oxide Catalyst to Activate Carbon Dioxide to Form Dimethyl Carbonate Monitored by Ce L3-edge XAFS

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Introduction
The importance of catalytic conversion of CO₂ into harmless, useful compounds is recognized again in relation to environmental problem. We recently reported photocatalytic conversion of CO₂ into methanol [1]. If the unreacted CO₂ is catalytically coupled with produced methanol to form dimethyl carbonate (DMC), CO₂ 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 CO₂ and methanol was investigated in mild reaction condition, e.g. 373 K and 1 MPa. The best catalyst was Cu/CeO₂, pre-reduced at 673 K. The reason why this catalyst worked well was investigated by using Ce L3-edge XAFS.

Methods
CeO₂ was synthesized by the addition of ammonia to CeIII 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 CO₂ and methanol in an autoclave was transferred to the air-tight Pyrex glass cell and transported to beamline. Ce L3-edge XAFS spectra were measured at 290 K at beamline 7C, 9A, or 9C in transmission mode.

Results and Discussion
CeO₂ produced DMC with the rate of 0.44 mmol h⁻¹ g⁻¹ cat at 393 K and 3.5 MPa (CO₂ 2.9 MPa; methanol 0.64 MPa). The rate was improved to 0.70 mmol h⁻¹ g⁻¹ cat in the same reaction condition over CeO₂ pre-reduced at 673 K in H₂.

In a milder reaction condition at 393 K and 1.3 MPa (CO₂ 0.67 MPa; methanol 0.64 MPa), DMC formation rate was 0.41 mmol h⁻¹ g⁻¹ cat using pre-reduced CeO₂ at 673 K in H₂.

The Ce L₁-edge XANES spectra for CeO₂-based catalysts and a reference are depicted in Figure 1A. Typical twin peaks appeared at 5731.9 and 5738.7 eV for as-synthesized CeO₂ (a) and the pattern was similar to that for (NH₄)₂CeIV(NO₃)₆ (the spectrum not shown), indicating the contribution of Ce IV. In contrast, single, more intense peak appeared at 5727.4 eV for CeIII(NO₃)₃·6H₂O (d).

Then, spectra b and c for pre-reduced CeO₂-x and pre-reduced Cu/CeO₂-x were fit with the combination of data for as-synthesized CeIVO₂ and CeIII(NO₃)₃·6H₂O 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 III sites was 10% upon reduction of CeO₂ at 673 K and the reduction to Ce III was promoted further to 20% with the doped Cu.

The catalytic DMC formation rates increased linearly as the partial pressure of CO₂ increased (0.13–2.9 MPa) for pre-reduced Cu/CeO₂-x catalyst. Reduced CeIII sites were suggested to adsorb CO₂ and the probability of nucleophilic attach of methoxy on the carbon of CO₂ increased.

References

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