

Mechanochemically-Treated Ceria: Surface Characterizations and Catalytic Production of Dimethyl Carbonate

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Abstract

Recently the direct synthesis of dimethyl carbonate (DMC) from carbon dioxide (CO₂) and methanol (CH₃OH) over cerium oxide (CeO₂) catalysts has drawn massive attention for its usage of CO₂ as reactant and absence of toxic reagents in the process. Commercial CeO₂ submicroparticle (SMCeO₂) is generally inexpensive while much less catalytically active than commercial CeO₂ nanoparticle. In this study, to enhance the catalytic activity for direct synthesis of DMC from CO₂ and CH₃OH of SMCeO₂, we have treated SMCeO₂ by ball milling. Reaction testing shows that ball milling of SMCeO₂ could significantly increase the DMC yield from 6 to 378 μmol g-cat⁻¹ h⁻¹, and further air calcination of ball-milled SMCeO₂ leads to a higher DMC yield of 538 μmol g-cat⁻¹ h⁻¹. Oxygen K-edge, cerium M-edge, and cerium L-edge X-ray absorption spectra (XAS) carried out at beamline BL20A and BL17C show that the number of oxygen vacancies at CeO₂ surface increases after ball milling. *In-situ* temperature-dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results indicate that mechanochemically-generated surface oxygen vacancies are beneficial for CO₂ activation. The air calcination decreases the adsorption strengths of both CO₂-derived (*i.e.*, bidentate carbonate) and CH₃OH-derived adspecies (*i.e.*, on-top methoxy) to facilitate the production of DMC. These results demonstrate that mechanochemical treatment is an efficient approach to synthesize active CeO₂ catalysts from inexpensive CeO₂ precursors.

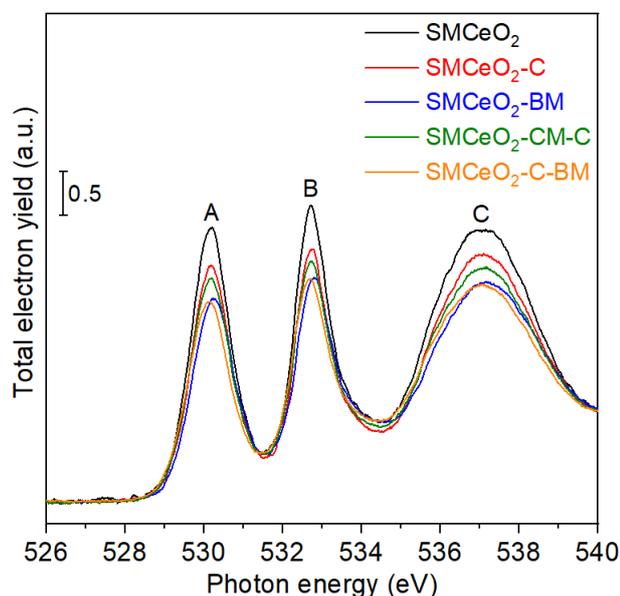


Figure 1. Oxygen K-edge XANES spectra of ball-milled and calcined derivatives of CeO₂ catalyst.

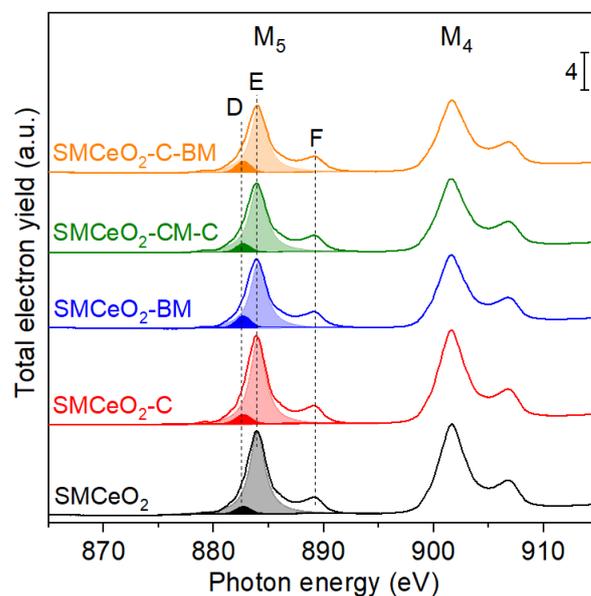


Figure 2. Cerium M_{5,4}-edge spectra of untreated, treated with ball milled and calcined CeO₂ catalysts.

Keywords: CeO₂, mechanochemical synthesis, CO₂ utilization, XANES, DRIFTS