

# Elucidating the role of metal oxides interaction and oxygen vacancy defects in tuning methanol and DME selectivity during CO<sub>2</sub> hydrogenation

## Abstract

To satisfy the energy demand of an increasing population fossil fuel reserves are being exploited at an unprecedented rate. The burning of these fossil fuels produces CO<sub>2</sub>, which is the main constituent of greenhouse gases and leads to global warming. Therefore, use of CO<sub>2</sub> as feed for methanol and DME production can be a possible route to close the anthropogenic carbon cycle. The reverse water gas shift reaction (RWGS) poses a major challenge to the design of methanol selective catalyst. Recently oxygen deficient catalytic systems like In<sub>2</sub>O<sub>3</sub>, ZnO-ZrO<sub>2</sub> and Zn<sub>2</sub>Ga<sub>2</sub>O<sub>4</sub> have been documented to be very selective for methanol synthesis reaction even at high temperature (300°C). The oxygen defective sites are helpful in CO<sub>2</sub> adsorption and activation. However, the catalytic activity of the oxygen deficient catalytic system is low due to absence of metallic sites for H<sub>2</sub> adsorption. Studies reporting interaction between the metallic Cu and oxygen deficient supports, and its consequence in the catalytic performance are few.

In this regard, a comparative study to investigate the role of oxygen vacancies and basic site density in tuning methanol selectivity during CO<sub>2</sub> hydrogenation over Cu/CeO<sub>2</sub>, CuZrO<sub>2</sub> and Cu/ZnO catalyst was performed. The catalysts were prepared by constant pH co-precipitation method and their catalytic performance was evaluated in a fixed bed tubular reactor. The methanol selectivity over Cu/CeO<sub>2</sub> catalyst reaches 90% at 220°C, 30 bar and 2400 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. The abundance of oxygen defects on the Cu/CeO<sub>2</sub> catalyst surface facilitates formation of unidentate carbonate species, which leads to selective methanol synthesis. The concentration of the oxygen vacancies was altered by preparing Cu/CeO<sub>2</sub> catalyst with co-precipitation, surfactant assisted co-precipitation and sol-gel method. The improved catalytic activity of Cu/CeO<sub>2</sub> catalyst prepared by sol-gel method is ascribed superior physicochemical properties like Cu surface area, small Cu particle size, strong basic site density and oxygen vacancy defects. The H<sub>2</sub>-TPR and XPS results confirms partial reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. This reduced CeO<sub>2</sub> promotes CO<sub>2</sub> adsorption and activation. The maximum methanol space time yield (STY) for Cu/CeO<sub>2</sub>-SG catalyst was 70.8 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 30 bar, 260 °C, 7200 mL kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and CO<sub>2</sub>:H<sub>2</sub> ratio 1:3. CeO<sub>2</sub> was incorporated as promoter into the conventional Cu/ZnO catalyst and for a constant Cu wt% (70 wt%), the ratio of Zn/Ce was optimized. The catalytic activity of Cu/ZnO/CeO<sub>2</sub> catalyst reached maximum for Zn/Ce ratio (wt/wt) of 2:1 and methanol STY was 100.4 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 30 bar, 250°C, 3000 mLg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and 1:3 H<sub>2</sub>/CO<sub>2</sub> ratio. The kinetic

data was measured within 220°C-280°C temperature, 10-40 bar pressure, 1800-3000 mL<sub>g<sub>cat</sub></sub><sup>-1</sup> h<sup>-1</sup> WHSV and 1:2, 1:3 and 1:4 CO<sub>2</sub>:H<sub>2</sub> ratio. The dual site LHHW model with formate hydrogenation as the rate determining step fitted well to the experimental results.

The major challenge for DME synthesis is excess water produced in the methanol dehydration deactivates catalytic performance. To address this issue mildly hydrophobic ZrO<sub>2</sub> is used as promoter to the Cu/ZnO catalyst. The synergistic effect between Cu, Zn and Zr oxides leads to higher DME selectivity and consequently inhibits the side reactions over the bifunctional catalyst. The ZnO-ZrO<sub>2</sub> interaction leads to formation of oxygen defective sites and improves the activity of bifunctional catalyst. The DME selectivity reaches up to 60% with 14% CO<sub>2</sub> conversion at 30 bar, 260°C, 2400 mL<sub>g<sub>cat</sub></sub><sup>-1</sup> h<sup>-1</sup> and 1:3 CO<sub>2</sub>/H<sub>2</sub> ratio. Altogether the tuning metal oxide interactions and oxygen vacancy defects is the key to enhance methanol yield by CO<sub>2</sub> hydrogenation.