

Continuous Catalytic Conversion of Carbon Dioxide to Chemical Fuels and *Operando* Spectroscopic Investigations

Besides the great advances in CO₂ sequestration technologies, CO₂ utilization and, particularly, artificial “carbon-recycling” have gained considerable attention to close the carbon cycle which has presently an open end due to the slowness of converting CO₂ into biomass and fossil fuels by natural processes. One of the most promising paths to convert a large amount of captured CO₂ is its catalytic conversion to useful and especially largely demanded chemicals like fuels. In this presentation, two unique approaches we have taken for efficient continuous catalytic conversion of CO₂ to chemical fuels will be presented together with spectroscopic investigation of the catalyst materials under working “*operando*” conditions.

In the first part, high-pressure approach (up to 500 bar) to synthesize methanol by means of CO₂ hydrogenation to benefit from both kinetics and thermodynamics will be described, yielding outstanding catalytic performance of >95% CO₂ conversion with >98% methanol selectivity with the highest methanol weight time yield reported to date. Also, our attempts to learn about the electronic state of active metal (Cu) by X-ray spectroscopy under *operando*, high-pressure and high-temperature, conditions will be described. Furthermore, *operando* visual inspection of catalyst and deactivation mechanism will be presented during the high-pressure synthesis of another CO₂ conversion reaction, dimethyl carbonate (DMC) synthesized from CO₂ and methanol over CeO₂ using an organic dehydrating agent. The work clearly shows that seeing (visually) is worth more than a number of catalytic tests to understand and optimize the catalytic process.

In the second part, our recent attempts to combine CO₂ capture and reduction processes by means of unsteady-state operation will be described, targeting at the synthesis of pure syngas from diluted CO₂ (flue gas). Catalytically active sites and species in the reaction were elucidated by space- and time-resolved DRIFTS, XAFS, and XRD to gain holistic views on the catalyst materials and also chemical gradients along the catalyst bed.