

EPFL Valais/Wallis SEMINAR

16. 06. 2020, 17:00 – 18:30, EPFL Valais/Wallis ZOOM PhD Public Defense

Mechanisms of the Heterogeneously Catalyzed Reaction of CO₂ Hydrogenation on Transition Metal Surfaces

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Renewable energy supply and energy storage in a closed materials cycle are the urgent global challenges of the 21st century. Carbon dioxide (CO₂) hydrogenation over transition metal catalysts is a method to produce synthetic fuels from renewable energy in a CO₂ neutral cycle. The methanation reaction, which is the primarily fully hydrogenated carbon reaction, proceeds in multiple reaction paths on a solid catalyst. It is crucial to understand the active sites and the related reaction mechanisms of CO₂ hydrogenation in order to improve the efficiency and selectivity of the reaction. However, the proposed mechanisms from literatures have been controversial due to two main difficulties in 1) evidently identifying the reaction species, especially some vital transient species on the pathway of carbon hydrogenation and C-C coupling, and 2) proving the relation between surface structure of the catalysts and the reactivities. To address these difficulties, we developed new instrumental setup (Diffuse Reflectance Infrared Fourier Transform Spectroscopy-Mass Spectroscopy-Gas Chromatography) and analysis program (Bi-level Evolutionary Gaussian Fitting) to investigate the catalyzed reaction on the catalyst surface in operando. Based on these developed methods, an investigation of the reaction mechanisms of CO₂ hydrogenation on a model catalyst, Ru/Al₂O₃, demonstrates the roles and pathways of each adsorbed species on the catalyst surface during the whole reaction. Inspired by those findings, we synthesized a new catalyst, Co_x(CoO)_{1-x}, in situ with high activity in CO₂ methanation reaction, and unraveled the functions of the metal and the metal oxide in the catalytic process.

References:

1. Zhao, K. *et al.* In Situ Control of the Adsorption Species in CO₂ Hydrogenation: Determination of Intermediates and Byproducts. *J. Phys. Chem. C* **2018**, *112*, 20888.
2. Zhao, K. *et al.* Identifying Reaction Species by Evolutionary Fitting and Kinetic Analysis: An Example of CO₂ Hydrogenation in DRIFTS. *J. Phys. Chem. C* **2019**, *123*, 8785.
3. Zhao, K. *et al.* Unraveling and optimizing the metal-metal oxide synergistic effect in a highly active Co_x(CoO)_{1-x} catalyst for CO₂ hydrogenation. *J. Energy Chem.* **2021**, *53*,241.
4. Zhao, K.; *et al.* A Combined Diffuse Reflectance Infrared Fourier Transform Spectroscopy-Mass Spectroscopy-Gas Chromatography for the *Operando* Study of the Heterogeneously Catalyzed CO₂ Hydrogenation over Transition Metal-Based Catalysts. *Rev. Sci. Instrum.* **2020**, under review.



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