Summary of Doctoral Thesis

"Heterogeneous Catalysis for CO_2 Valorization: Catalyst Studies and Infrared Spectroscopy."

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1. Introduction

Carbon dioxide (CO_2) valorization through catalytic hydrogenation can simultaneously mitigate emissions and produce fuels and chemical intermediates when renewable hydrogen (H_2) is available. In this context, CO_2 hydrogenation to methane represents a key Power-to-Gas route, enabling compatibility with natural-gas infrastructures and, potentially, acting as an energy carrier for hydrogen. CO_2 hydrogenation to methanol is an alternative pathway that yields a versatile platform molecule for chemicals and fuels. This thesis investigates heterogeneous catalysts for both routes and uses *in situ* and *operando* infrared (IR) spectroscopy as a central tool to connect catalyst formulation, surface chemistry, and performance.

2. CO_2-to-methane

For CO_2-to-methane, the target product is directly compatible with the existing natural-gas value chain and can support renewable-energy storage. Methanation is thermodynamically favored but kinetically limited and therefore requires active catalysts, typically based on Ni or Ru and operated at moderate-to-high temperatures; under these conditions, the reverse water-gas shift (RWGS) remains the main competing pathway, producing CO that can also participate in subsequent hydrogenation steps. These aspects motivate a detailed investigation of operating parameters and of the catalyst/support interplay to maximize CH_4 selectivity while limiting RWGS. So, a benchmark 1 wt.% Ru/Al_2O_3 catalyst was first tested in fixed-bed reactors to quantify how temperature, feed composition, and space velocity affect activity, selectivity, and competition with RWGS. Subsequently, a library of low-Ru catalysts supported on different oxides was investigated by combining catalytic evaluation with physicochemical and morphological characterization (BET, XRD, STEM-EDX, and temperature-programmed analyses) to rationalize structure-performance relationships. Composition screening highlighted the decisive role of the support and identified low-loading Ru/TiO_2 as a particularly promising formulation (*1*).

Operando DRIFTS and complementary transmission FTIR were employed to follow surface species under working feeds and to support mechanistic interpretation. On Ru/TiO_2, carbonate and bicarbonate species dominate at low temperature, while a weak band around 1991 cm^{-1}, attributed to linearly adsorbed CO, appears under reaction mixtures. Switching to more, reducing feeds increases CO_2 conversion above 90% while maintaining CH_4 selectivity above 99%, and combining IR and online mass-spectrometric evidence indicates only a minor RWGS contribution at the highest temperatures.

3. OPL-aware DRIFTS methodology

Because diffuse-reflectance spectra are intrinsically sensitive to optical artifacts, a methodological part of the thesis develops an optical-pathlength (OPL) assessment for DRIFTS using $CaCO_3$ as an internal standard, tracking characteristic $CaCO_3$ bands (e.g., near 1795 and 2510 cm^{-1}). The study shows that temperature ramps and, especially, redox activation can markedly modify the effective sampling depth as catalysts become more absorbing upon reduction. A practical workflow is proposed to monitor and compensate OPL variations during activation and reaction, enabling robust comparison of operando spectra across pretreatments and materials (*2*, *3*).

4. CO_2-to-methanol and zeolite investigations

For CO_2-to-methanol, the thesis builds on the industrial relevance of methanol as a versatile feedstock and on the fact that catalyst selectivity is governed by the balance between CO_2 activation, hydrogenation kinetics, and competing pathways (e.g., CO formation via RWGS and dehydration routes leading to DME). In addition to conventional Cu-based catalysts, indium oxide has emerged as a high-performing material for CO_2-to-methanol, emphasizing the role of oxide redox chemistry and oxygen vacancies in stabilizing CO_2-derived intermediates (*4*). For In_2O_3-based ZrO_2-supported systems, hydrogen activation sites have been identified as a key descriptor for methanol synthesis under CO_2 hydrogenation conditions (*5*).

Catalyst development and benchmarking were therefore combined with physicochemical characterization (BET, XRD, STEM-EDX, TPR/TPD) and *operando* transmission FTIR in a high-temperature/high-pressure cell. A catalyst library including Cu-Ce oxides (also prepared via exsolution), Cu/ZrO_2 with different Cu loadings, In_2O_3/ZrO_2, and $Cu\text{-}In_2O_3/ZrO_2$ were tested under pressurized conditions (up to 23 bar, 200-300 °C), highlighting trade-offs between activity and methanol selectivity. Cu-rich Cu/ZrO_2 maximized the CO_2 conversion rate, whereas $Cu\text{-}In_2O_3/ZrO_2$ improved methanol selectivity and stability relative to In_2O_3/ZrO_2. For In_2O_3/ZrO_2, *operando* FTIR supports the formation of CO_2-derived intermediates and underlines the need to control pretreatment severity to avoid over-reduction toward inactive metallic indium. These investigations complement earlier work on In-Cu binary oxides for CO_2 hydrogenation (*6*).

Operando IR spectroscopy provides additional interpretative handles for selectivity and by-product formation. In methanol adsorption experiments, methoxy species form readily on Cu/ZrO_2, while under CO_2 hydrogenation conditions, carbonate and formate signatures dominate, consistent with a formate-related reaction network. The spectroscopic trends, interpreted together with catalytic testing, help rationalize the emergence of by-products such as CO and DME and clarify how catalyst composition and pretreatment influence surface coverage under working conditions.

Finally, the thesis establishes a quantitative transmission FTIR protocol based on CD_3CN adsorption to compare Brønsted and Lewis acidity in ZSM-5 zeolites. The resulting workflow provides a reproducible mapping of acid-site distributions that is directly relevant to downstream methanol-valorization chemistry (e.g., acid-catalyzed upgrading steps, including DME-related pathways) and supports the broader goal of designing integrated concepts for CO_2 conversion and upgrading.

5. Conclusion

Overall, the thesis combines catalyst structure-performance studies with IR-based methodological advances that strengthen mechanistic interpretation under working environments. The integrated approach enables rational comparison among catalyst formulations for CO_2 methanation and CO_2-to-methanol under representative conditions, while also improving the reliability of *operando* DRIFTS analyses when optical properties evolve during activation and reaction.

6. References

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