Summary

The urgent need to mitigate anthropogenic CO_2 emissions while ensuring energy security has positioned Carbon Capture Utilisation and Storage (CCUS) technologies as a benchmark for the global energy transition.

In the framework of CCU, this thesis investigated the catalytic hydrogenation of CO_2 into high-value energy carriers through two primary pathways: Power-to-Methane (PtM) and Power-to-Liquid (PtL). By integrating advanced catalyst synthesis, multi-scale characterisation and process simulation, this work addresses the fundamental challenge of coupling catalyst architecture and process design to overcome kinetic and thermodynamic barriers in circular carbon systems.

The work combines experimental catalysis with process-level thermodynamic and kinetic analysis. In the PtM pathway, CO_2 methanation was studied using both conventional steady-state operation and integrated carbon capture and utilisation (ICCU) strategies. Ni-supported on ultra-stable Y (USY) zeolites demonstrated optimal performance, in particular with an exceptional resistance to coke formation. The study also revealed that the hierarchical porosity of the zeolite framework and the size of metal particles are critical aspects governing catalytic behaviour of catalysts, with performance driven by particle size and dispersion rather than by thermodynamic constraints. Furthermore, rhenium-based dual-functional materials enabled temporally decoupled CO_2 capture and conversion steps, achieving 100% methane selectivity and demonstrating that the synergy between catalytic sites and adsorbent functions can effectively bypass the selectivity limitations of conventional continuous processes.

In contrast, CO_2 hydrogenation to methanol revealed different constraints related to thermodynamics. Cu-based catalysts showed methanol selectivity only within a tight temperature range (150 – 200°C), beyond which the reverse water-gas shift (RWGS) and methanation reactions became dominant, proving that process optimisation relies on catalysts characteristics, such as a precise control of the metal-support interface, which can be effectively tuned by the choice of metal precursor. This behaviour reflects the intrinsic thermodynamic limitation of methanol synthesis, where higher temperatures improve kinetics but disfavour equilibrium conversion. Process simulations were performed with Aspen Plus® and demonstrated that single-pass adiabatic reactors are inherently limited, achieving low CO_2 conversion and methanol yield, whereas syngas recycle significantly enhanced overall performance, increasing CO_2 conversion to ~75% and methanol yield to ~65% without altering catalyst formulation.

Exploratory screening of Cu-Fe-Ce and Cu-Fe catalysts at elevated pressure showed predominant selectivity toward CO and CH_4 rather than methanol, but they are interesting for further and deeper investigations. These findings confirm that catalyst selectivity is controlled by the combined effects of metal composition, redox behaviour, and operating regime, and that methanol synthesis requires catalyst architectures specifically tailored to its requirements.

Overall, the thesis demonstrates that effective CO_2 utilisation cannot rely on catalyst development alone. For PtM, flexibility in catalyst-process coupling enables operation under diverse regime, including dynamic conditions. For PtL, stringent thermodynamic constraints necessitate precise catalyst design supported by advanced reactor configurations. This work contributes to the progress in CO2-based e-fuel technologies providing novel insights in the integrated approach including catalysts development and process engineering, providing a framework for rational design of future circular carbon systems.