

Summary of Doctoral Thesis

**"Development of dual function materials (DFMs) with low-ruthenium content for cyclic methanation of CO<sub>2</sub>"**

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This research focuses on the development and optimisation of Dual Function Materials (DFMs) designed for the cyclic adsorption and *in-situ* catalytic conversion of carbon dioxide (CO<sub>2</sub>) into synthetic natural gas (CH<sub>4</sub>) via the Sabatier reaction. DFMs, composed of adsorbent and catalytic components, were synthesised and evaluated to determine their methanation performance.

Ruthenium–ceria composite materials were prepared using a sequential impregnation technique. Cerium oxide was dispersed in varying concentrations (10, 20, and 30 wt.%) onto two different supports—zeolite H-ZSM-5 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>—to assess CO<sub>2</sub> adsorption capacities under various thermal conditions (150, 200, and 250 °C) at atmospheric pressure. The materials exhibiting the highest adsorption capacity, 30%CeO<sub>2</sub>/ZSM-5 and 30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, were subsequently impregnated with 2 wt.% Ru to form the active catalytic phase. Comprehensive characterisation of these materials was performed using techniques such as XRD, N<sub>2</sub> physisorption at -196 °C, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, ICP-MS, XPS, FESEM, HRTEM, and FT-IR.

Catalytic tests were carried out at 250 °C to simulate flue gas conditions, maintain consistency with adsorption parameters, and prevent side reactions, particularly the reverse water–gas shift (RWGS), which can reduce CH<sub>4</sub> yield. The Ru-loaded DFMs exhibited complete selectivity towards methane, with CO<sub>2</sub> conversion governed by the stoichiometric H<sub>2</sub>:CO<sub>2</sub> ratio of 4:1. Multiple adsorption-methanation cycles were conducted to evaluate material stability and reusability. The 2%Ru/30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> material maintained a consistent CO<sub>2</sub> uptake (ranging from 101 to 123  $\mu\text{mol g}^{-1}$ ) and an average CH<sub>4</sub> yield of 90%. In contrast, 2%Ru/30%CeO<sub>2</sub>/ZSM-5 showed higher CO<sub>2</sub> uptake (up to 359  $\mu\text{mol g}^{-1}$ ) but lower conversion efficiency, with a maximum CH<sub>4</sub> yield of 32%, attributed to the enhanced adsorption capability of the zeolite support not translating into effective catalytic conversion.

Further work addressed the development of Ru-based catalysts supported on MgO and Mg–Al, optimised for integration into Power-to-Gas (PtG) systems. These catalysts, formulated with a low Ru loading (2 wt.%), were evaluated under both dry and humid conditions to reflect practical operational environments.

MgAl-supported catalysts demonstrated superior CO<sub>2</sub> adsorption compared to their MgO-based counterparts, owing to larger surface areas and a greater abundance of basic Mg<sup>2+</sup>–O<sup>2-</sup> sites. Doping with potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) enhanced surface alkalinity and CO<sub>2</sub> binding

strength, although it resulted in a decrease in surface area. The presence of water vapour further improved CO<sub>2</sub> uptake and methanation efficiency by promoting the formation of reactive carbonate species, especially on Ru/LDO and Ru-K/LDO catalysts. CH<sub>4</sub> production was significantly enhanced under humid conditions, with Ru-K/LDO reaching values up to 333 μmol g<sup>-1</sup>.

The analyses of methane profiles indicated that Ru-K/LDO exhibited slower methanation rates compared to Ru/LDO. This behaviour was attributed to stronger carbonate bonding, reduced Ru dispersion, and a lower surface area following K<sub>2</sub>CO<sub>3</sub> incorporation. *Operando* FTIR spectroscopy revealed mechanistic differences: Ru/LDO facilitated rapid conversion via bicarbonate intermediates, whereas Ru-K/LDO followed a pathway involving more stable formate and formyl species, accounting for the slower kinetics.

The results highlight the potential of Ru/LDO-based catalysts for industrial CO<sub>2</sub> capture and utilisation within PtG applications, combining high adsorption capacity, efficient reaction kinetics, and stable performance across cycles. Ru-K/LDO, although slower in conversion, offers superior CO<sub>2</sub> capture and may be advantageous in applications that allow for extended reaction durations.