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HYBRID TANDEM CATALYTIC CONVERSION PROCESS TOWARDS HIGHER OXYGENATE EFUELS

E-TANDEM - Deliverable report

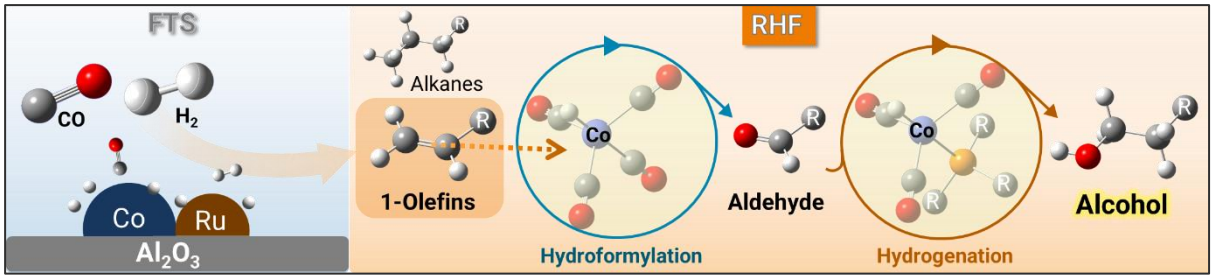
D2.2 Catalysis and hybrid process for syngas conversion to higher alcohol fuels

Project summary

E-TANDEM's ambition is to unlock an efficient and direct production of a new higher-oxygenate diesel-like e-fuel for the marine and heavy-duty transport sectors. This oxygenated fuel is directly produced from water, CO_2, as the sole carbon source, and renewable power as the sole energy input, in a once-through hybrid catalytic conversion process integrating three major catalysis branches: (1) high-pressure electrocatalysis syngas production coupled to a tandem catalytic e-syngas conversion, encompassing (2) thermocatalysis with solid catalysts and (3) chemocatalysis with molecular complexes. The project will demonstrate the new e-fuel production process at bench-scale, and assess its capacity to cope with fluctuating energy inputs.

Publishable summary

The E-TANDEM project aims to develop a lab-scale, single-step process for converting CO_2/H_2O co-electrolysis-derived syngas (e-syngas, H_2+CO) into synthetic higher alcohols through the tandem integration of olefin-selective Fischer-Tropsch synthesis (FTS) and olefin oxo-functionalization via reductive hydroformylation (RHF) at mild temperatures. This thermo-catalytic tandem process is central to the E-TANDEM concept for higher oxygenate e-fuels. Achieving this goal requires optimizing catalyst formulations and operating parameters in a single slurry-phase reactor. Initially, the focus will be on studying the individual catalysts for each conversion step under conditions relevant to the tandem process. This includes the development and optimization of cobalt-based solid catalysts for FTS, aimed at maximizing selectivity for higher (C_{4+}) 1-olefins as substrates for the RHF step. Additionally, the design of molecular RHF catalysts seeks the identification of cost-effective cobalt species stabilized by thermally robust mono- and bidentate organic ligands, capable of chemo- and regioselectively converting FTS-derived 1-olefins (C_n) into linear C_{n+1} alcohols *in situ*.



This report summarizes experimental findings on the optimization of solid and molecular catalysts for one-step e-syngas processing. It examines the influence of operational parameters on key performance metrics such as alcohol selectivity, productivity, and linear-to-branched ratios. Parameters studied include temperature, syngas pressure, solvent selection, $[Co]_{RHF}$: $[Co]_{FTS}$ molar ratios, and the nature of organic ligand stabilizers for the molecular catalyst. Particular attention is given to gas composition, as the e-syngas feed—sourced from an upstream CO_2/H_2O co-electrolysis step—contains unconverted CO_2 and water traces. Water is additionally produced in the FTS reaction, and therefore its effect on the overall tandem performance is of technical significance for catalyst and process optimization.

This report presents research findings from WP2, "Catalysts and Processes for Hybrid Catalytic Conversion of CO_2 and Water to Higher-Oxygenate e-Fuels (HOEF)," specifically addressing Deliverable 2.2 (D2.2) under Task 2.2. The primary objective of this task is to develop a laboratory-scale, carbon-efficient, single-step tandem catalysis process for converting co-electrolysis-derived syngas. The process integrates Fischer-Tropsch synthesis and olefin reductive hydroformylation functionalities, aiming for high selectivity (>50%) to higher alcohol products, syngas conversion >60%, mild operating temperatures (180 ±30°C), and productivities ≥200 mg g_{metal}^{-1} h^{-1}.

Significant progress has been made toward this goal. The best-performing system achieved a higher-alcohol productivity of 212 mg g_{metal}^{-1} h^{-1} at 200°C, surpassing the target. However, the maximum selectivity to higher (C_{2+}) alcohols reached approximately 42 wt%, falling slightly short of the

target. Continued optimization during the remaining project duration may close this gap. When target performance is achieved, an updated report will be submitted to the European Commission.

Additionally, the report details advancements in analytical methods. The complex product mixtures, comprising paraffins, olefins, and oxygenates across various chain lengths, necessitated customized analytical techniques, including two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2DGC-ToFMS). In addition, developing reaction setups capable of withstanding challenging conditions (T>473 K; P>18 MPa) and employing parallelized catalyst screening (HTS) techniques were central for the implementation of the research described in this report.