Project progress – D3.2. Initial lab-scale tests for plasma-catalytic methanol production
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This deliverable D3.2 "Initial lab-scale tests for plasma-catalytic methanol production" builds directly upon the catalyst work compiled in the parallel deliverable D3.6 "Catalyst advancements for methanol synthesis". This presents the first experimental results from testing those materials in a plasma-catalytic reactor and providing a critical assessment of the analytical methodologies commonly employed in the field.

The experimental campaign tested a series of Cu-based catalysts, including CuAl2O3, CuZSM-5 (prepared by ion exchange and incipient wetness impregnation), CuMCM-41, CuZnZSM-5, and the benchmark CuZnAl; in a temperature-controlled dielectric barrier discharge (DBD) reactor operating at atmospheric pressure. Catalyst screening revealed that, whilst Cu-based catalysts can moderately enhance methanol selectivity relative to the empty reactor, the reaction remains strongly dominated by the reverse water-gas shift (RWGS) pathway, producing primarily CO. Among all tested materials, CuZnZSM-5 exhibited the highest methanol selectivity (~1.6%), though this value remains far below what is commonly reported in the literature. Co-feeding experiments further demonstrated that methanol is highly susceptible to plasma-induced decomposition, with conversion exceeding 90% under typical operating conditions, which fundamentally limits net methanol production.

A critical outcome of this deliverable is the rigorous comparison between online and offline product analysis methodologies. Results clearly demonstrate that the offline approach widely used in the plasma-catalysis literature (which indirectly infers methanol selectivity from the residual carbon balance) can overestimate methanol formation by up to five-fold. Online gas chromatography measurements reveal significantly lower selectivities, highlighting a systematic analytical bias across the published literature. These findings are considered highly relevant to the broader research community and are being prepared for submission to the journal Chem Catalysis.

Overall, this deliverable establishes that the temperature-controlled DBD reactor configuration, as commonly employed in the field, is not well-suited to plasma-catalytic CO2 hydrogenation to methanol. Therefore, the plasma-based activaties in ALCHEMHY are shifting focus to the RWGS reaction. It also provides ALCHEMHY with an essential and rigorous baseline, and points towards future directions focused on improved plasma-catalyst contact through 3D-structured catalysts and surface DBD configurations, as well as optimised reactor design to minimise methanol decomposition.

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