213a - Separation Enhanced Thermochemical Reactions in a Fluidized and Entrained Flow Reactor

Abstract

1. **Introduction**

Fossil fuels represent ancient solar energy stored underground, formed over millions of years from plants that captured sunlight and CO_2 to produce hydrocarbons rich in chemical energy. When burned, these fuels release that stored energy, but also emit CO_2 back into the atmosphere. Today, it is important to design processes that synthesize renewable and energy-dense fuels as the world seeks to decarbonize energy systems [1].

To achieve carbon-neutral fuel synthesis, the CO_2 emitted during fuel combustion must equal the amount consumed during its production. Biomass offers options to replace fossil fuels, and CO_2 derived from biomass fermentation is a non-fossil carbon source for the synthesis of energy-dense carbon molecules [2]. The synthesis of such molecules from CO_2 requires its chemical reduction with hydrogen, which can be produced via renewable electricity-driven water splitting. One of the major challenges of this approach lies in the thermodynamic limitations of CO_2-based reactions, such as the reverse water-gas shift (CO production), direct dimethyl ether (DME) synthesis, methanol synthesis, and methanation [3]. The latter two enable the production of biofuels compatible with existing energy infrastructures: biomethane can be directly injected into the natural gas grid, while biomethanol can be used as a fuel in conventional gas turbines, blended with gasoline or diesel, serve as an intermediate for the synthesis of sustainable aviation fuels (SAF) and other chemicals, or act as a liquid carrier for hydrogen storage [4].

This project focuses on advancing reactor design for process intensification in CO_2-based fuel synthesis, with a focus on low-pressure methanol production. The proposed approach integrates continuous sorbent-assisted catalysis within a fluidized and entrained flow reactor, where sorbents are entrained through the fluidized catalyst bed to selectively remove reaction products in situ, and regenerated in a separate vessel. This configuration mitigates the equilibrium limitations of CO_2 conversion reactions, enhances product purity, and supports decentralized fuel synthesis by coupling renewable hydrogen with biogenic CO_2.

2. **Methods**

The performance of various sorbent materials, including zeolites (types Y, 3A, 4A, 5A, and 13X), is being experimentally investigated in terms of their water, methanol, and CO_2 co-adsorption capacities. Experiments are conducted at a lab-scale under a constant pressure of 3 bar and temperatures ranging from 200 to 300 °C, corresponding to the active

window of the Cu/ZnO/Al_2O_3 (CZA) catalyst used for methanol synthesis, the primary reaction of interest. Real-time gas composition and temperature monitoring are achieved using a mass spectrometer, NDIR sensor, and in-reactor thermocouples. The objective of the adsorption experiments is to identify sorbents capable of selectively removing reaction products and shifting equilibrium during CO_2 hydrogenation reactions at different temperatures and feed compositions to map sorbent performance and quantify product uptake, with particular focus on enhancing methanol yield. The dehydration of methanol is also investigated by quantifying DME and water formation during pure methanol adsorption.

Subsequently, methanol yields from both standard and sorption-enhanced (SE) methanol synthesis are measured between 3 and 30 bar to assess the potential of the selected sorbents. In parallel, fluidization tests with particle size distribution monitoring are carried out to confirm the mechanical stability of materials under conditions representative of the proposed intensified reactor design.

3. Results and discussion

Among the zeolites already investigated, only molecular sieve 13X showed measurable CO_2 adsorption, with a low capacity between 2 and 3%. Other zeolites (type Y, 3A, 4A, and 5A) showed no CO_2 uptake within the investigated temperature range. Competitive adsorption of methanol with subsequent formation of DME and water was observed for all sorbents except zeolite 3A. The latter, characterized by its smaller micropore diameter of 2.9 Å, demonstrated selective water adsorption behavior, highlighting its potential for use in steam-enhanced reactions, including biomethanol synthesis at low pressures. Despite the competitive adsorption of CO_2 and methanol, zeolite 13X exhibited the highest water adsorption capacity so far (above 9% at 220°C). All named sorbents showed a sharp decrease (more than 60%) in water uptake as temperature increased from 220 to 280 °C, as shown in Figure 1.

In parallel, steam-enhanced methanol synthesis using zeolite 3A was investigated in both fixed- and fluidized-bed reactors at pressures between 3 and 9 bar and temperatures of 220–250 °C. The experiments (up to 10 kW H_2 input) demonstrated a twofold increase in methanol output at the highest pressure and lowest temperature, exceeding the thermodynamic equilibrium for a small catalyst loading when the gas hourly space velocity was reduced. Significant CO formation was observed, with methanol selectivity improving by up to 36% as pressure increased from 3 to 9 bar, as shown in Figure 2. In the fluidized-bed configuration, only half the catalyst–sorbent bed was required to achieve the same enhancement observed in the fixed bed, accompanied by a sharper water breakthrough that could facilitate sorbent entrainment for regeneration. This suggests that the potential

of the separation-enhanced fluidized and entrained flow reactor lies in entraining the sorbent bed before saturation to maintain continuous enhancement and maximize production. Additionally, an isothermal temperature profile was maintained throughout operation. However, a reduction in particle size distribution was detected for both catalyst and sorbent, indicating the need for developing more mechanically stable materials. These findings support the ongoing development of new catalyst–sorbent blended materials and intensified reactor configurations for applications such as SAF synthesis and a closed-loop supercritical gas turbine system operating on renewable fuels, currently being designed within the EU HERMES project.

4. Conclusions

The use of entrained-bubbling fluidized beds combines the advantages of sorption enhancement and improved temperature control in smaller reactor volumes. Further to improving methanol yield, this can be achieved with continuous, thus facilitated, operation. Offering promising insights on sustainable energy carriers, the presentation will showcase experimental results of SE methanol synthesis, together with a complete matrix of adsorption experiments comparing the performance of the already tested zeolites and other materials for CO_2 hydrogenation reactions. Some sorbents will be selected for experimental extrapolation of Langmuir parameters to support methanol reactor modeling.

5. References

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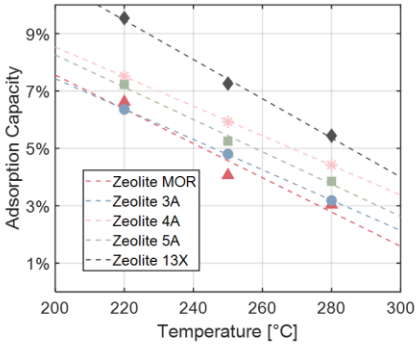

Figure 1. Water adsorption capacity measured in this work for single water adsorption (20 mol.% H_2O in Ar at 220-280 °C) over zeolites Sodium Mordenite (MOR), 3A, 4A, 5A and 13X.

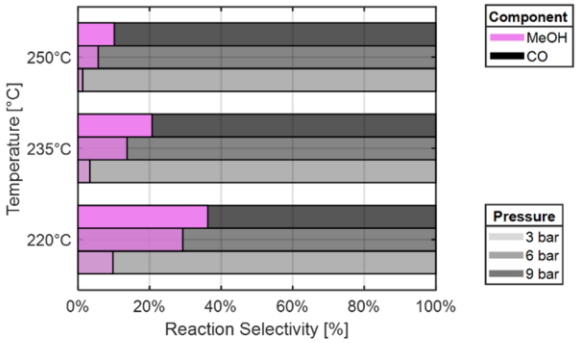

Figure 2. Methanol vs CO production selectivity during water sorption enhancement in a CO_2-based methanol reactor filled with CZA catalyst and operating between 3-9 bar and 220-250 °C.