Enhanced methanol synthesis by sorbent circulation

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Highlights

- Sorption capacity of five zeolites for water, methanol and CO2 was investigated.
- Zeolites MOR, 3A, 4A, 5A, and 13X were tested from 200 – 280°C.
- Both fixed bed and fluidized bed sorption enhanced methanol synthesis was tested up to 30 bar.
- Fine sorbent material can be circulated through catalyst particles in bubbling fluidization.

1. Introduction

The synthesis of carbon-neutral fuels such as methane, methanol or DME 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.

This project focuses on advancing reactor design for process intensification in CO_2-based fuel synthesis, with a focus on low-pressure methanol synthesis [1]. The proposed approach integrates continuous sorbent-assisted catalysis within a fluidized and entrained flow reactor [2], where sorbents are entrained through the fluidized catalyst bed to selectively remove reaction products in situ and regenerated in a separate vessel [3]. 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, (zeolites MOR, 3A, 4A, 5A, and 13X) is experimentally investigated in terms of their water, methanol, and CO_2 co-adsorption capacities. Experiments are conducted at a lab-scale at pressures from 3 bar to 30 bar and temperatures ranging from 200 to 280 °C, corresponding to the active window of the $Cu/ZnO/Al_2O_3$ (CZA) catalyst used for methanol synthesis. The objective of the adsorption experiments is to quantify product uptake, deviation from equilibrium in reverse water gas shift reaction and methanol synthesis. The dehydration of methanol is also investigated by quantifying DME and water formation during pure methanol adsorption.

In parallel, fluidization tests with different particle size distributions are conducted in a bench scale cold flow model representative of the proposed intensified reactor design to confirm the possible window of operation parameters for varying material properties (especially particle diameters) of catalyst and sorbent particles.

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 MOR, 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 sorption-enhanced reactions at low pressures. Despite the competitive adsorption of CO_2 and methanol, zeolite 13X exhibited the highest water adsorption capacity. 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, sorption-enhanced methanol synthesis using zeolite 3A was investigated in both fixed- and fluidized-bed reactors at pressures between 3 and 30 bar and temperatures of 220–250 °C. The experiments (up to 10 kW H_2 input) demonstrated a more than twofold increase in methanol compared to the thermodynamic equilibrium output at the highest pressure and lowest temperature. This suggests that the potential of the separation enhanced fluidized bed reactor lies in entraining the sorbent bed before saturation towards a regenerator to maintain continuous enhancement and maximize production.

The fluid-dynamic cold-flow experiments showed that it is indeed possible to circulate fine sorbent material through a bed of larger catalyst particles in bubbling fluidization. The possible combinations of Geldart A and Geldart B particles were investigated for a wide range covering particle diameters from 63 to 1000 micrometers.

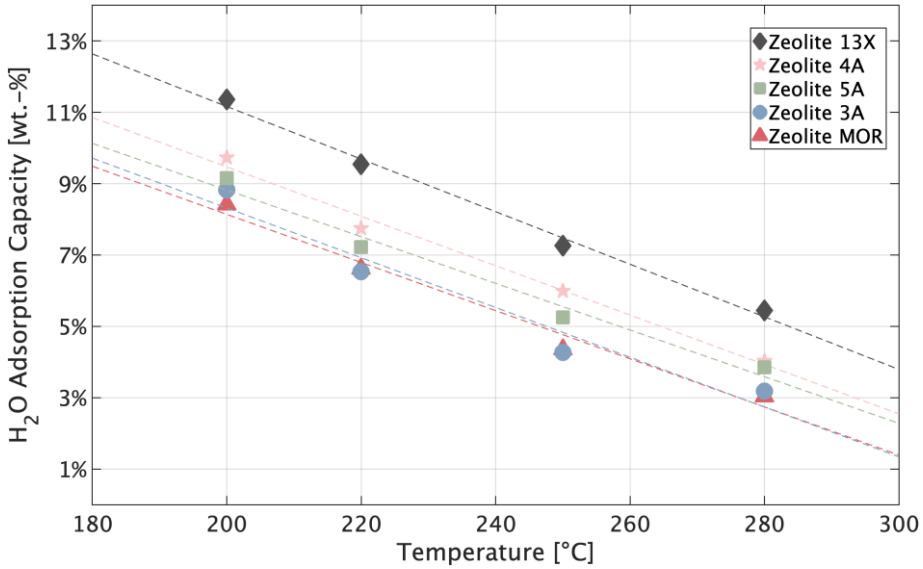

Figure 1. Water adsorption capacity of different sorbents as function of the temperature at 0.6 bar partial pressure of H_2O

4. Conclusions

It could be demonstrated that sorption enhancement allows to increase the yields in methanol synthesis beyond thermodynamic equilibrium. This is especially beneficial when starting from CO_2 and in decentral plants where cost limitation favors low pressure processes. Continuous entrainment of sorbent from the reactor to a regenerator is possible and allows to optimize both the methanol synthesis reactor in bubbling fluidized bed regime and the sorbent regeneration in a separate vessel. Further, the batchwise regeneration of the sorbents within the reactor can be omitted leading to more compact reactor designs.

References

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Keywords

Sorption-enhancement, methanol synthesis, zeolite, fluidized bed reactor, fixed bed