

INTENSIFIED METHANOL AND DIMETHYL ETHER SYNTHESIS BY IN-SITU WATER REMOVAL USING HYDROPHILIC MATERIALS

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Abstract

The synthesis of methanol (MeOH, an important feedstock in chemical industry and specialized fuel) and dimethyl ether (DME, potential alternative to Diesel fuel with high energetic efficiency and low emissions of NO_x and CO) by CO₂ hydrogenation is an efficient way to reduce the important emissions of this major contributor to the greenhouse effect, as well as an alternative to CO₂ sequestration by chemical recycling. However, the conventional syntheses do not allow to obtain appropriate conversions for industrial applications, even at high pressures and using improved catalysts. Intensifying the hydrogenation process by application of hybrid configurations combining the reaction system with selective in-situ separations (sorption-enhanced process, SEP) can lead to a very efficient CO₂ catalytic conversion. In this work, innovative MeOH and DME sorption-enhanced syntheses at both low and high pressure are investigated. Hydrophilic water selective sorbents were used for in-situ water removal from the reaction media to evaluate experimentally the application of the SEP in a fixed-bed reactor. The experimental data were compared with the simulated results obtained with a two-scale, isothermal, unsteady-state model. Selective in-situ water removal allows to increase CO₂ conversion, MeOH and DME yields and DME selectivity even performing the process at low pressures, thus becoming an industrially attractive process of CO₂ valorization.

Keywords

CO₂ conversion, Hydrophilic sorbents, Methanol, Dimethyl ether, In-situ water removal.

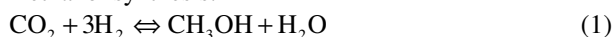
Introduction

Methanol (MeOH) is mainly used as a key feedstock in chemical industry, as fuel for specialized vehicles and for the production of fuel additives components. The industrial synthesis from a gas mixture CO/CO₂/H₂ is usually carried out over Cu/ZnO/Al₂O₃ catalyst at high pressures (between 50 and 100 bar) (Waugh, 2012). Dimethyl ether (DME) is a potential alternative to Diesel fuel with high energetic efficiency and low emissions of NO_x and CO. DME is traditionally produced by MeOH dehydration over acid catalysts. By the increase of CO₂ concentration in the atmosphere, which is known to mainly contribute to the climate change, the CO₂ capture concept has recently attracted a considerable interest to mitigate industrial CO₂ emissions (IPCC, 2014). CO₂ capture leads to concentrated

streams for sequestration or further use. MeOH and DME syntheses by CO₂ hydrogenation are efficient ways to reduce the important emissions of this major contributor to the greenhouse effect, as well as an alternative to CO₂ sequestration by chemical recycling (Centi and Perathoner, 2009; Olah et al, 2006).

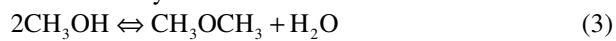
MeOH and DME syntheses from CO₂ involves the following reactions with high synergy degree (direct DME synthesis involves two steps: MeOH synthesis followed by in-situ methanol dehydration):

Methanol synthesis:





Methanol dehydration:



Reverse water gas shift (RWGS):



DME synthesis from CO_2 can be performed in a single high-pressure reactor (single-step) by using a bifunctional catalyst for MeOH synthesis & dehydration (i.e., Cu-ZnO- Al_2O_3 /HZSM-5). A relatively large amount of water is produced in these processes through the reactions (1), (3) and (4). Continuous in-situ water removal while it is produced in the reaction media leads to the increase of CO_2 conversion through the reactions (1) and (3), the increase of MeOH yield through the reactions (1) and (2) and the increase MeOH conversion toward DME through the reaction (4). Compared to MeOH, DME synthesis from CO is thermodynamically favored (Centi and Perathoner, 2009). CO_2 conversion towards DME is therefore a very challenges process. Combining reaction with in-situ water separation is therefore an effective way to eliminate thermodynamic limitations.

Our recent numerical evaluation on CO_2 conversion to DME (dimethyl ether) synthesis revealed that water removal increased MeOH and DME yields, and DME selectivity (Iliuta et al., 2011). Moreover, the process efficiency increases at higher CO_2 feed concentration, thus favoring the use of CO_2 in the hydrogenation process. The development of efficient hydrophilic materials for in-situ water separation under specific reactive conditions (temperatures far from ambient, simultaneous presence of gases and vapors, and high pressures) represents the key element in this hybrid process. The objective of this work is to investigate experimentally the efficiency of innovative intensified MeOH and DME syntheses at low- and high-pressure conditions by in-situ water removal using developed specific hydrophilic materials. The performance of both synthesis reactors was also evaluated by employing a two-scale, isothermal, unsteady-state model and compared to the experimental data.

Experimental

The adsorption kinetics of high-temperature water sorbent materials developed in our laboratory was determined using the Intelligent Gravimetric Analyser IGA-003 (Hiden Isochema). The catalytic reaction was performed in a fixed-bed reactor fed with mixtures of water selective hydrophilic sorbents based on zeolite materials and inorganic salts and corresponding catalysts, in a range of temperature and pressure of 463-523K and 1-50 bars, respectively. Outlet composition was determined using a TCD/FID chromatograph.

Modeling

The two-scale, isothermal, unsteady-state model developed in our previously work (Iliuta et al., 2011) and used to evaluate the performance of MeOH and DME synthesis reactors and was compared with the experimental data.

Results

Several important results were obtained in the work; the most important are summarized here. Performing the processes with in-situ water removal is more efficient in comparison with the traditional fixed bed reactor at both low and high pressures. The acceleration of RWGS step by in-situ water removal improves significantly the CO_2 conversion. The increase of in-situ water removal accelerates the dehydration reaction in DME synthesis due to reduced kinetic inhibition by water; it therefore reduces the fraction of unconverted methanol and the result is the increase/decrease of DME/MeOH selectivity. Under in-situ water removal (sorbent volume fraction up to 0.5), water mole fraction in the gas is negligible, accelerating methanol production and increasing CO_2 conversion. Under H_2O removal conditions, methanol and DME yields increase with the increase of CO_2 concentration in the feed ($\text{CO}/\text{CO}_2/\text{H}_2$). The increase of sorbent volume fraction improves MeOH dehydration and increases therefore DME selectivity especially at high CO_2 feed concentration.

Conclusions

Selective in-situ water removal in MeOH and DME syntheses allowed to increase CO_2 conversion, MeOH and DME yields and DME selectivity even performing the process at low pressures, thus becoming an industrially attractive process of CO_2 valorization.

Acknowledgments

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