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Kinetic Study of Methanol and Direct Dimethyl Ether Synthesis from CO_2 rich Syngas

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Highlights

- Direct conversion of CO_2-rich synthesis gas to dimethyl ether (DME) on a commercial $Cu/ZnO/Al_2O_3$ catalyst has been investigated at different experimental conditions.
- The experimentally received product compositions were modeled numerically using key steps such as methanol formation, water gas-shift and methanol dehydration.
- The kinetic model fits the experimental CO conversion and the yield of DME over the studied range of conditions

1. Introduction

The current need for dependable and renewable energy sources has led to a diversified energy matrix. However, the fluctuating nature of the renewable resources highlights the relevance of efficient, carbon neutral energy storage solutions [1, 2]. Dimethyl ether (DME) is a suitable chemical energy carrier that can be manufactured via the conventional route in two steps, first the synthesis of methanol commonly using a Cu/ZnO-based catalyst, followed by methanol dehydration over an acid support. DME can be produced directly in one step using a bifunctional catalyst or a mixture of Cu/ZnO-based catalyst and dehydration sites. Single-step method requires only one reactor and it can also decrease the thermodynamic limitation of methanol synthesis by converting it in-situ into DME [3]. The key to optimize a catalytic process in order to maximize its viability lies in a better understanding of the mechanism behind the reaction. In this work, we present a kinetic study for the single-step DME synthesis. The kinetic parameters were estimated based on a proposed model [4] and our own experimental results.

2. Methods

Within this study, the direct synthesis of DME was investigated in a fixed-bed reactor. A mixture 1:1 of a commercial catalyst for methanol synthesis $Cu\text{-}ZnO\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ for selective methanol dehydration to DME was used. The reactor was filled with 2 g of catalysts (1 g each type) diluted with a ratio 1/5 with SiC for a better temperature distribution. The kinetic experiments have been carried out under the following reaction conditions: 493-533 K; 50 bar; modified residence time (τmod) 4.3-16.4 g*s/ml; initial gas-composition between H2:CO:CO_2:inert = 38:15:1:46 and 19:4:3:74.

3. Results and discussion

The DME synthesis from H_2:CO:CO_2 can be described using three reactions: methanol formation ($CO + 2\ H_2 \leftrightarrow CH_3OH$), methanol dehydration ($2\ CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$) and reverse water-gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$). Kinetic parameters were calculated for each of the above mentioned reactions using a kinetic model proposed in the literature [4] and the experimental results obtained for the single steps.

An example of one of our kinetic measurements for direct DME synthesis from syngas is shown in Figure 1. The dashed lines represent the equilibrium at the given conditions, while the continuous lines and the symbols represent the experimental results and the simulation respectively. The residence time is defined in terms of mass of catalyst over inlet volume flow rate and is called modified residence time (τmod). It can be seen that CO conversion as well as DME yield rises with increasing modified residence time τmod and temperature.

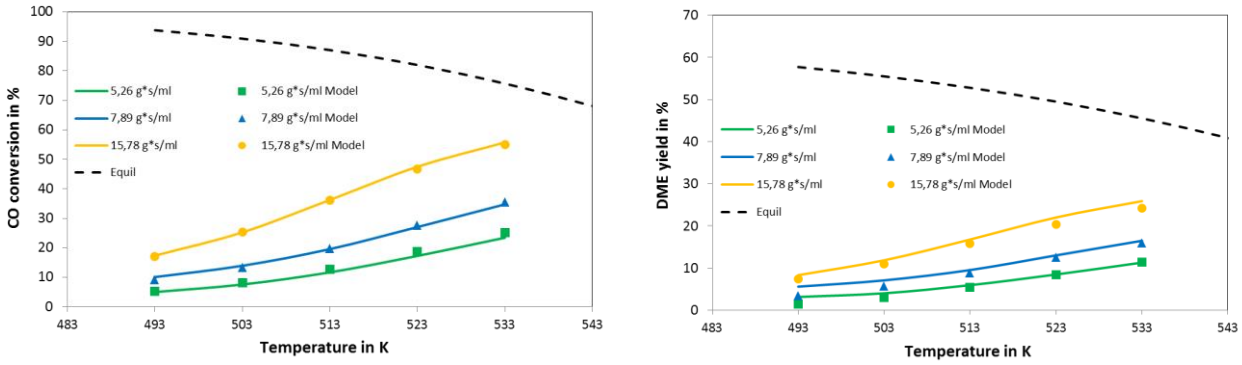

Figure 1. Influence of temperature and modified residence time (τmod) on CO conversion and DME yield during direct DME synthesis, H2:CO:CO_2:inert = 22:8:1:69, 50 bar

4. Conclusions

The direct synthesis of DME was investigated experimentally. Based on a published model and the measured data, the influences of different factors, such as temperature, residence time and CO_2-concentration in the inlet feed are simulated and analyzed. The kinetic data obtained in this work can be used to predict the reactor behavior by numerical methods, which becomes a useful diagnostic tool to enhance the process efficiency.

References

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Keywords

dimethyl ether; syngas; fixed-bed reactor; kinetics