

# EXPERIMENTAL AND SIMULATION STUDY OF DIMETHYL ETHER SYNTHESIS FROM SYNGAS ON A COMMERCIAL Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> CATALYST

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## Abstract

Direct conversion of synthesis gas (CO/H<sub>2</sub>) to dimethyl ether (DME) on a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst has been investigated. The kinetic measurements were performed using an isothermal fixed-bed reactor within wide operating conditions: 493-533 K; 50 bar total pressure, H<sub>2</sub>:CO-ratio of 1 in the feed and modified residence times ( $\tau_{\text{mod}}$ ) between 8.5-70 kg\*s/mol. A kinetic model proposed in the literature was correlated with the experimental results obtained in this study. 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 conversion of CO and the carbon-based selectivity to DME and CO<sub>2</sub> over the studied range of conditions.

## Keywords

dimethyl ether, syngas, fixed-bed reactor, kinetic parameters

## Introduction

Increasing global warming and the high demand of oil supply have encouraged the search for alternative fuels. Dimethyl ether (DME) synthesis has gained considerable attention in the field of catalysis, as a potential clean fuel for diesel engines due to its high cetane number and low NO<sub>x</sub> and CO emissions after combustion, in comparison with liquefied petroleum gas (LPG).

The conventional route for DME synthesis is through methanol dehydration over an acid support (e.g.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Industrial practice commonly relies on Cu/ZnO-based catalyst for methanol production from H<sub>2</sub> rich syngas (CO/H<sub>2</sub>), this process can be coupled with reforming of natural gas. The utilization of biomass gasification turns the produced DME in a “biofuel” (Dahmen et al. 2012; Rostrup-Nielsen 2000). However, the reaction to produce methanol from syngas is limited by thermodynamic equilibrium especially at high temperatures which results in a significant decrease in the conversion (Sun et al.

2014). DME can also be produced directly from syngas in one step using a bifunctional catalyst or a mixture of Cu/ZnO-based catalyst and an acidic catalyst. The main advantage of this method is the lower thermodynamic limitation in comparison with methanol synthesis. The amount of water in the system is lowered though the water-gas shift reaction (WGSR) causing higher syngas conversion (Peng et al. 1999).

In this work, we present an experimental study for DME synthesis in a single step. The kinetic parameters were estimated based on a proposed model (Aguayo et al. 2007) and our own experimental results.

## Experimental Section

Within this study, DME synthesis in a single step was investigated in a fixed-bed reactor. The reactor consists of a stainless steel tube with an inner diameter of 12 mm and

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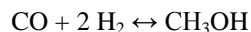
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420 mm length. A thermocouple, which can be placed at different axial positions, is used to measure the temperature. Details of the experimental setup can be found elsewhere (Henrich et al. 2015). A physical 1:1 mixture of a commercial catalyst for methanol synthesis Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for selective methanol dehydration to DME was used. The reactor was filled with 4 g of catalysts (2 g each type) diluted with a ratio 1/10 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 ( $\tau_{\text{mod}}$ ) 8.5-70 kg\*s/mol; initial gas-composition H<sub>2</sub>:CO:N<sub>2</sub>:Ar = 15:15:10:60. The product stream was analyzed by GC equipped with a TCD and FID (Agilent G1530A) and a ShinCarbon ST column (Restek).

## Results and Discussion

The DME synthesis from CO/H<sub>2</sub> can be described using three reactions:

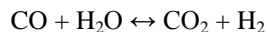
Methanol formation:



Methanol dehydration:



Water-gas shift reaction:



The kinetic model proposed by Aguayo et. al (Aguayo et al. 2007) based on the above mentioned reactions was correlated with the experimental results obtained in this study. Kinetic parameters were calculated based on the proposed model and the experimental results. The equilibrium calculations were performed with the software Aspen Plus®. All model equations were implemented in MATLAB. Figure 1 shows the influence of the temperature on CO conversion at different modified residence time ( $\tau_{\text{mod}}$ ). The dashed line represents the equilibrium at the given conditions, while the symbols and the continuous lines represent the experimental results and the simulation respectively for CO conversion. It can be seen that the conversion rises with increasing  $\tau_{\text{mod}}$  and temperature. However, at 533 K the conversion decreases in comparison with 523 K caused by the influence of the thermodynamics. As conversion is close to the thermodynamic equilibrium, reaction rate slows down.

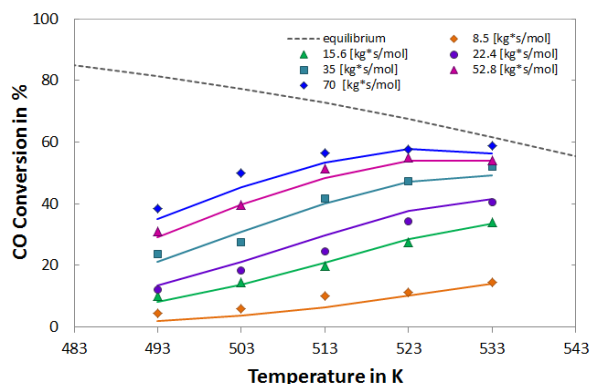


Figure 1. Influence of temperature on CO-conversion.

Figure 2 shows the influence of the temperature on DME and CO<sub>2</sub> selectivity. The selectivity of both species remains nearly constant. These results are closed to the theoretical maximum values for DME (67 %) and CO<sub>2</sub> (33 %), which is also an indicator that the in situ dehydration of methanol is complete.

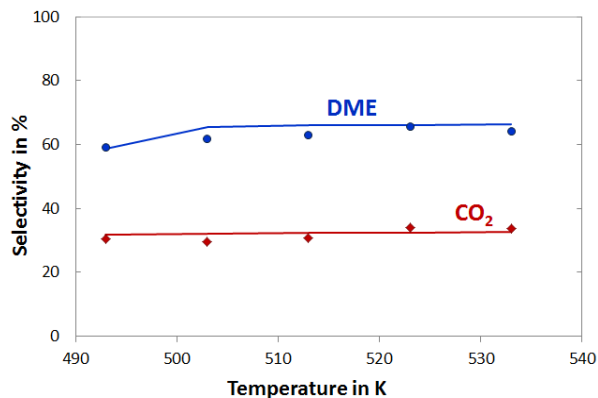


Figure 2. Influence of temperature on selectivity

## Conclusion

The direct synthesis of DME was investigated experimentally. At higher temperature and long residence times the influence of the thermodynamic equilibrium is significant. Based on a published model and the measured data, the influences of different factors, such as temperature and residence time are simulated and analyzed.

## References

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