**Catalytic Performance Investigations of the Direct DME Synthesis with Variable CO/CO2/H2 Feeds.**

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**Highlights**

* Highly active CZZ/zeolite catalyst system with high CO2 tolerance
* Good long-term stability under variable operating conditions

**1. Introduction**

Synthesis gas, a mixture of H2, CO and CO2 with variable composition, is the preliminary stage for many basic chemicals. Synthesis gas can be produced from a variety of feedstocks, resulting in a wide range of CO/CO2/H2 ratios[1]. Methanol (MeOH) and Dimethylether (DME) formed from synthesis gas are promising energy carriers in the “Power to Fuels” (PtF) concept[2]. Using CO2 as a COx source would lead to a CO2 recycle system and to CO2-neutral fuels.

**2. Methods**

Within this study, the direct DME synthesis is investigated in a fixed-bed reactor aiming at dynamic processing with variable feed compositions. For initial methanol formation Cu/ZnO/ZrO2 (CZZ) catalysts prepared at KIT-IKFT/TVT are used. Different solid-acid components such as γ-Al2O3, H-FER and H-MFI realize the dehydration of MeOH to DME. Experiments have been carried out under following reaction conditions: 483-523 K; 50 bar; gas hourly space velocity (GHSV) between 18.000 and 42.000 mlN/(g\*h); initial CO2/(CO2+CO) inlet-ratio between 0 and 1.

**3. Results and discussion**

Figure 1 (left) shows that CZZ catalyst enables up to 76 % higher DME productivity compared to a commercial Cu/ZnO/Al2O3 (CZA) sample material. DME productivity can be even increased at 503 K by raising the CO2 content in the feed. At higher reaction temperature, the thermodynamic equilibrium becomes more noticeable, reflected by lower DME productivity for CO2-rich feed compositions. More CO2 in the feed generally favors water formation by reverse water-gas shift reaction, what also leads to a reduction of DME productivity[3]. In a long-time experiment over nearly 600 h time on stream (ToS) using a CZZ/H-FER catalyst system a total decrease of 29 % in DME yield is observed. Figure 1 (right) shows the deactivation during the first 100 h under constant reaction conditions, followed by periods of variable dynamic changes subjected to varying temperatures, residence times and feed compositions.

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**Figure 1.** DME productivity of CZZ/H-FER and a commercial CZA/H-FER catalyst system (left). DME yield in a long time test of the CZZ/H-FER system (right).

**4. Conclusions**

The CZZ/H-FER system prepared at IKFT shows an enhanced performance compared to a commercial CZA/H-FER system and is a promising material for the conversion of syngas to DME with variable composition of CO/CO2/H2. With the appropriate choice of reaction conditions it is possible to make the DME productivity almost independent of the CO2/(CO2+CO) inlet-ratio.

**References**

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