

## Direct DME synthesis over bifunctional catalysts: preparation and characterization of a core@shell system

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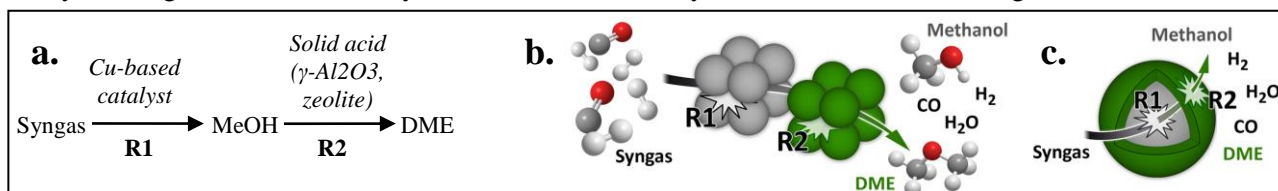
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### Highlights

- The concept of one-stage DME synthesis *via* core@shell catalysts is presented.
- CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>@zeolite catalysts were prepared and characterized.
- Focus on MeOH core catalyst synthesis via flame spray pyrolysis and spray drying.

### 1. Introduction

In the scenario of the energy transition the conversion of renewable electricity into fuels and chemicals is widely discussed (power-to-X technologies). One option is the conversion of hydrogen (from water electrolysis) together with CO and/or CO<sub>2</sub> into dimethyl ether (DME) *via* methanol (MeOH) as an intermediate product (Fig. 1a). The process leads to the production of an excellent, efficient alternative to diesel fuel, with almost smoke-free combustion [1]. In case of small scale, decentralized applications the major drawback of the conventional two-stage DME synthesis (Fig. 2b) is the thermodynamic limitation of CO-conversion ( $X_{CO}$ ). To overcome the low  $X_{CO}$  equilibrium, the one-stage synthesis of DME from synthesis gas in microstructured reactors is a promising process: the coexistence of the both catalysts in the reactor allows to shift the MeOH synthesis equilibrium by its direct dehydration to DME; by a core@shell catalyst configuration, a selectivity to DME of theoretically 100 % can be reached (Fig. 1c) [2, 3].



**Fig. 1:** a) Reactions for the DME synthesis from synthesis gas over b) two sequential steps and c) core@shell catalytic system

This contribution presents the preparation of core@shell catalysts, focusing on the core synthesis, as a successful zeolite shell synthesis requires mechanically stable core particles bigger than 20  $\mu\text{m}$ , in order to avoid any alteration during the process. Moreover, the influence of a whole as well as a partial zeolite shell coverage is discussed.

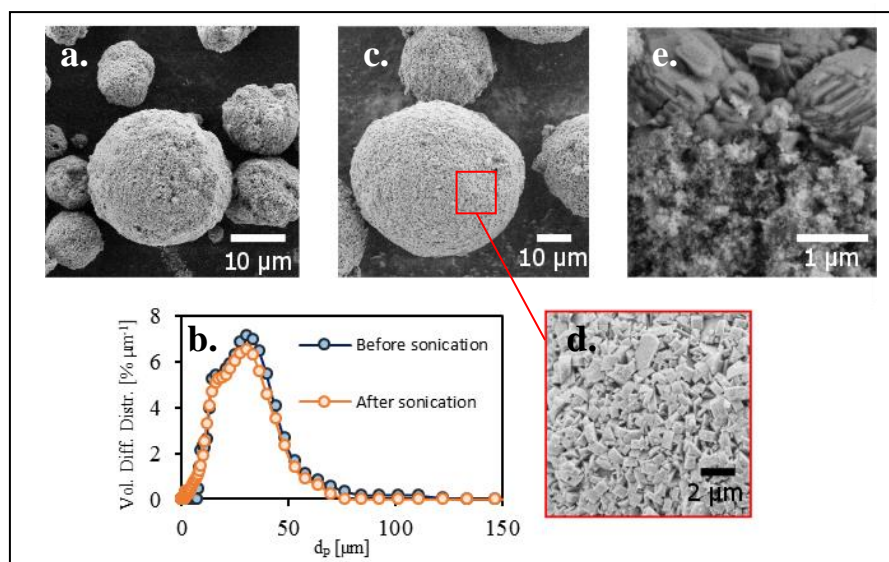
### 2. Methods

The CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is prepared *via* semi-continuously flame spray pyrolysis (FSP-CZA). Nitrate salts dissolved in pure ethanol are fed into a nozzle and dispersed using oxygen. The FSP-CZA is collected by a bag-house filter. The proper core size is reached by (a) agglomerating the calcined FSP-CZA *via* spray drying (SD-CZA), or b) pelletizing and grinding the FSP-CZA (P-CZA). The shell was synthesized *via* a two-step hydrothermal synthesis procedure of in-situ seeding and secondary growth. By adjusting the synthesis parameters of the second synthesis step, the final shell was either dense, obtaining SD-c@s (from SD-CZA) and P-c@s (from P-CZA), or not fully intergrown with a zeolite partial coverage (SD-c@n-s). The influence of calcination on the FSP-CZA is studied with XRD and TPR. SD-CZA is characterized analyzing its sphericity (SEM) and mechanical resistance by measuring the particle size distribution before and after

ultrasonic treatment (static light scattering). The presence of a dense zeolite layer and its thickness is investigated by SEM. P-CZA, SD-c@s and SD-c@n-s were tested in a  $\mu$ Berty reactor.

### 3. Results and discussion

The FSP in combination with the bag-house filter enabled a constant production rate of up to 20 g day<sup>-1</sup> of catalyst powder. Fig. 2a shows the SEM picture of the spray dried SD-CZA. As shown in Fig. 2b, *via* ultrasonic treatment the mechanical stability of the catalyst was confirmed, as only a negligible difference of the core size distribution is visible after sonication. Both core materials, SD-CZA and P-CZA, have successfully been enwrapped by a zeolite shell which covers the whole surface (e.g. Fig. 2d). In the case of P-CZA the coating process is much easier in terms of handling the material due to the larger particle size. Fig. 2e shows the SD-c@n-s catalyst: both CZA and zeolite are accessible from the surface. From the catalytic tests the FSP-CZA shows activity for the MeOH synthesis ( $X_{CO}$  of 8.9 and 10.6 % for the calcined P-CZA and the P-CZA respectively; the reference commercial catalyst showed 17.7 %). The lower activity of the calcined catalyst for the MeOH synthesis is due to the increase of the primary particle size (result also confirmed by XRD and TPR). The SD-c@s catalyst showed  $X_{CO}$  of only 1.7 % with no DME detectable, while for the SD-c@n-s catalyst  $X_{CO}$  of 6.5 % was reached and DME was produced, which indicates a more difficult diffusion of the components in presence of a dense shell.



**Figure 2:** a) SEM of the spray dried core catalyst SD-CZA and b) its particle size distribution before and after ultrasonic bath; SEM pictures of c) SD-c@s catalyst d) zoom on the shell surface, e) zoom on the external surface of the SD-c@n-s catalyst

### 4. Conclusions

Core@shell catalysts for the direct DME synthesis from synthesis gas have been successfully synthesized. The CZA nanopowder was prepared *via* semi-continuous FSP. Starting from spray dried FSP-CZA as well as from ground pellets the particles could be successfully covered by a zeolite shell. By adjusting the synthesis parameters, the coverage grade of the shell was varied. The reaction tests showed higher  $X_{CO}$  in the case of non-dense zeolite shell. Ongoing work focuses on the understanding of the influence of the diffusion for the two cases as well as on comparing the activity for the P-c@s catalyst.

### References

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### Keywords

“single-stage DME synthesis”; “core@shell”; “flame spray pyrolysis”; “spray drying”