Catalytically coated POCS for reaction kinetic studies in a Berty-type reactor for the FORMOX process

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Motivation

For heterogeneously catalyzed gas phase reactions, packed bed reactors are the state of the art. However, these systems suffer from reduced radial heat conduction, resulting in temperature maxima within the catalyst bed for exothermic reactions. This comes along with the risk of thermal runaway, catalyst deactivation and a lower product selectivity. An option for process intensification is the utilization of a continuous solid metal matrix, so called periodic open cellular structures (POCS), instead of a randomly packed bed, which enhances radial heat and mass transfer based on the geometry of the structure [1]. Busse et al. showed for the example of the FORMOX process that the packed bed can be replaced by catalytically coated POCS, which leads to a lower hot spot temperature and consequently to a lower side product selectivity [2]. These carrier structures are predefined, regular and offer additional degrees of freedom, e.g. the geometry of the unit cell, which enable a model-based optimization of the reactor. In this regard, Littwin et al. established a corresponding model for heat transport for diamond unit cell-based POCS [3]. For describing the kinetics in an integral reactor with catalytically coated structures, an adapted model is being derived on the basis of an intrinsic kinetic model, taking into account the influence of the coating and the support structure.

Materials and methods

For the determination of the mass transport influence on coated structures, many parameters have to be considered and validated. They can be classified into the geometrical and morphological design of the structure, the coating of the structures, and the reaction conditions during the kinetic measurements.

The process of the manufacturing is shown in Figure 1. For the structures, the flatly designed POCS are additively manufactured via fused filament fabrication with a *BASF Ultrafuse* 316L filament and subsequent sintering to stainless steel structures at inert atmosphere. For the coating of the support structure, the catalyst, which mostly contains iron molybdenum oxide $Fe_2(MoO_4)_3$, is being suspended in ethanol and grinded to a median particle size of 5 µm. Subsequently, it is being dip coated on the support and calcinated at 500 °C for 24 h.

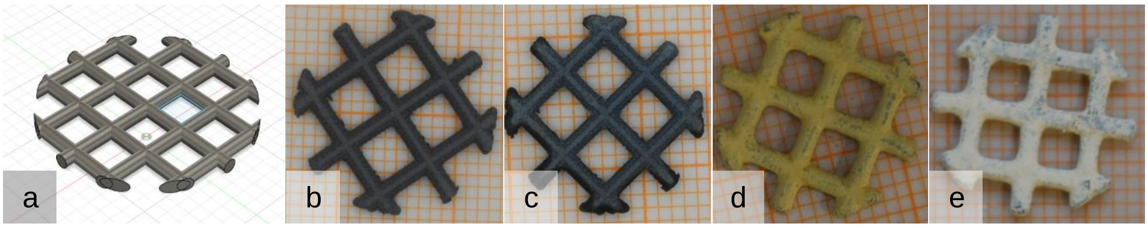

Figure 1*: Exemplary processing of the coated POCS manufacturing. a: CAD-file of planar POCS. b: Additively manufactured raw product by fused filament fabrication. c: Sintered metallic structure. d: Structure coated with Fe-Mo-catalyst (before calcination). e: Catalytically active coated structure after calcination for kinetic measurements.*

The measurements of the effective gas phase kinetics are carried out in a gradient-free Berty-type reactor, with a feed varying from 8 - 10 vol.-% methanol and 10 to 12 vol.-% oxygen at temperatures from 250 to 375 °C and atmospheric pressure. The analysis of the products formed is implemented via GC with TCD and FID to sensitively detect all possible products formed.

Residence time distribution measurements with CO_2 as inert tracer material provides information over the dispersive mass transport and is performed prior to the kinetic measurements.

Results and conclusion

When considering methanol conversion and formaldehyde yield of the catalytically coated structures in comparison to kinetic measurements with a powder bed, it can be shown that the same amount of catalyst leads to lower conversion. The parameters, which are of major interest for this observation are the catalyst mass, the specific surface area of the coating (BET measurement), the average coating thickness, and the morphology of the POCS, which is defined by its geometry. Thereafter, a parameter sensitivity study is carried out to determine the influence of the aforementioned parameters on the reaction kinetics and fit the measured data to an adapted kinetic model. For ongoing research, the adaptability of this model to three dimensional catalytically coated supports has to be checked.

References

[1] A. Inayat et al., Chem. Eng. Sci., 2011, 66, 2758-2763.

[2] C. Busse, Dissertation, FAU Erlangen-Nürnberg, 2020.

[3] G. Littwin et al., Ind. Eng. Chem. Res., 2021, 60 (18), 6753 – 6766.