Diamond unit cell-based POCS as catalyst in the FORMOX process: Experimental investigations and reactor simulation studies

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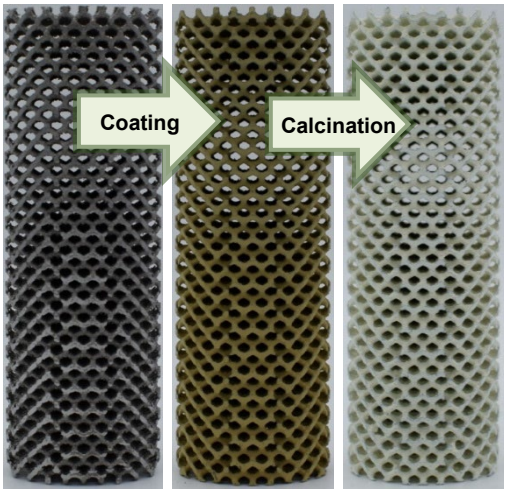
Introduction

The partial oxidation of methanol to formaldehyde is a highly exothermic, heterogeneously catalyzed gas-phase reaction. In industrial practice, in the FORMOX process iron-molybdate oxide catalyst pellets are applied as random packing in a tubular fixed-bed reactor. Due to limited heat transport within the packed particle bed, overheating can occur inside the reactor, leading to increased catalyst deactivation and the formation of side products. By introducing a continuous solid matrix instead of a random catalyst particle bed, heat conduction improves, resulting in both lower hotspot temperatures and reduced selectivity for side products [1]. These periodic open cellular structures (POCS) feature a defined unit cell geometry, which enables precise numerical investigations of their regular morphology as well as experimental studies of the additively manufactured structures [2]. The application of POCS as a catalyst carrier and the validation of established correlations are essential for accurately predicting reaction and reactor behavior.

Methods and results



The experimental investigations were performed in a lab-scale reactor system featuring a tubular reactor with an inner diameter of 3 cm. The reactor was equipped with precise temperature control, enabling wall temperatures to be maintained within the range of 250 to 400 °C in the catalytic zone, which spanned a length of 10 cm. The feed gas mixture consisted of methanol (up to 10 vol.-%), air, and nitrogen as an inert carrier gas to ensure stable reaction conditions. Additively manufactured periodic open cellular structures (POCS) composed of Ti-6Al-4V (Ti64) alloy, with

varying unit cell geometries, were employed as structured supports. These POCS were coated with a catalytically active iron-molybdate-oxide layer to facilitate the partial oxidation of methanol. Reaction products—including formaldehyde, dimethyl ether, methyl formate, methylal, carbon monoxide, and carbon dioxide—were quantified using gas chromatography (GC) equipped with both thermal conductivity (TCD) and flame ionization detectors (FID).

The experimental results were analyzed by comparison with a one-dimensional pseudohomogeneous reactor model, including an intrinsic reaction kinetic model using a Mars-van Krevelen approach, which accounts for the redox mechanism of the iron-molybdate catalyst. Internal mass transport limitations were neglected based on residence time investigations of the coated structures, supporting the validity of assuming a nonporous catalyst coating. Heat transport within the diamond unit cell POCS was modeled using an established correlation [3, 4].

Discrepancies between experimental data and model predictions were observed in terms of product distributions, indicating an offset in selectivity and activity of the catalyst compared to those predicted by the kinetic model. Additionally, axial dispersion effects on mass transport demonstrated divergences from idealized assumptions inherent to the model, leading to the necessity of adapting the model. A more precise prediction of reactive behavior enables model-based optimization approaches for this system, with the POCS geometry as a degree of freedom.

References

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