

PREPARATION AND PERFORMANCE OF A CATALYST COATED STACKED FOIL MICROREACTOR FOR THE METHANOL SYNTHESIS

Xuyen Kim Phan¹, Hamidreza Bakhtiary D.¹, Rune Myrstad², Janina Thormann³,
Peter Pfeifer³, Hilde J. Venvik^{1*}, Anders Holmen¹

¹ Department of Chemical Engineering, Norwegian University of Science and
Technology (NTNU), N-7491, Trondheim, Norway

² SINTEF Materials and Chemistry, N-7465 Trondheim, Norway

³ Karlsruhe Institute of Technology, Institute for Micro Process Engineering, D-76344
Eggenstein-Leopoldshafen, Germany

Summary

A stacked foil microreactor (SFMR) was developed and used to study the methanol synthesis under high pressure. Two catalyst foil coatings were applied, Pd/CeO₂ by sol-gel coating + impregnation and CuO/ZnO/Al₂O₃ by co-precipitation + slurry coating. Laboratory fixed bed reactor (FBR) experiments were made for comparison. The results show that stable and active foil coatings of both Pd/CeO₂ and CuO/ZnO/Al₂O₃ can be prepared, but detailed understanding of the catalyst structure as well as SFMR reactor characteristics are needed to explain and further optimize these systems.

Keywords

Microreactor, methanol synthesis reaction, catalyst coating, Cu, Pd

Introduction

Microstructured reactors have received attention over the past two decades due to their process intensification and safety potential. This potential arises from the high surface to volume ratio that enhances mass and heat transfer, as well as from the small amount of reactants and products inside each microchannel. Using microchannels for heterogeneously catalyzed reactions introduces new challenges to catalyst loading, since filling the microchannels with catalyst powders may lead to flow maldistribution. For the option of coating the microchannel walls with catalytic materials, heat and mass transfer properties may allow coatings with even higher activity than powder filling. However, a considerable increase of surface area relative to the channel geometric area, accompanied with good adhesion on the channel walls, is demanded for the coatings. This study focuses on a microreactor configuration of stacked, catalyst coated foils for the methanol synthesis. Two catalytic coatings were prepared, Pd/CeO₂ and CuO/ZnO/Al₂O₃, and studied under relevant conditions. A comparison to laboratory scale fixed reactor experiments has also been made.

Experimental

The stacked foil microreactor (SFMR) was made by Karlsruhe Institute of Technology (KIT), and consisted of fourteen structured foils. The foils were equipped with 200 μm x 200 μm microchannels and 100 μm thick fins

between these. Each foil contained 50 channels of 150 mm length. The structured and coated foils were stacked in a stainless steel housing, using SK graphite seals (Frentzelit) to allow for high pressure. The SFMR was heated electrically by 16 cartridges to maintain a uniform temperature profile, which was recorded by insertion of thermocouples into holes in the SFMR outer shell.

For the Pd/CeO₂ coating, a CeO₂ sol-gel was prepared according to N. Oezer et al.¹, dripped uniformly over the microchannels, dried at 70 °C overnight and calcined at 500°C for 5hrs in air. The CeO₂ layer was then impregnated with a PdCl₂ solution until obtaining 10%Pd/CeO₂, and dried and calcined as before. CuO/ZnO/Al₂O₃ was prepared by a two-step coprecipitation method according to the ICI procedure² and slurry coated onto the foils as described elsewhere.³

Pd/CeO₂ and CuO/ZnO/Al₂O₃ catalysts were reduced in 10 vol.% hydrogen in nitrogen at 300 °C and in a premixed (H₂/CO/CO₂/N₂) syngas at 250 °C, respectively. The premixed syngas was fed at varying contact time (GHSV), 80 bar and 220-300 °C reaction temperature. For fixed bed experiments, a Pd/CeO₂ powder was prepared by deposition – precipitation.⁴ Undiluted 50-120 μm particles of Pd/CeO₂ or CuO/ZnO/Al₂O₃ were used.

For comparison of SFMR and FBR performance, the maximum catalyst temperature (peak) along the FBR axis has been compared to the mid-section SFMR temperature.

* To whom all correspondence should be addressed. E-mail: hilde.venvik@chemeng.ntnu.no

Results and discussion

Pd/CeO₂ showed high initial activity in the methanol synthesis in both reactor types, even exceeding the methanol synthesis equilibrium conversion in the case of the SFMR. This could be explained by a high initial activity for methane formation ($S(\text{CH}_4)_{300\text{ }^\circ\text{C}} = 50\%$) not considered in the equilibrium calculation. The activity decreased significantly over time to stabilize the conversion after ~100hrs on stream (Figure 1) with significantly lowered methane selectivity ($S(\text{CH}_4)_{300\text{ }^\circ\text{C}} = 17\%$). The reaction proceeded up to 400 hrs without further deactivation. Figure 1 also shows higher conversion for the Pd/CeO₂ catalyst coated on foils and employed in the SFMR than for the Pd/CeO₂ catalyst particles in the FBR, presumably due to the different preparation techniques.

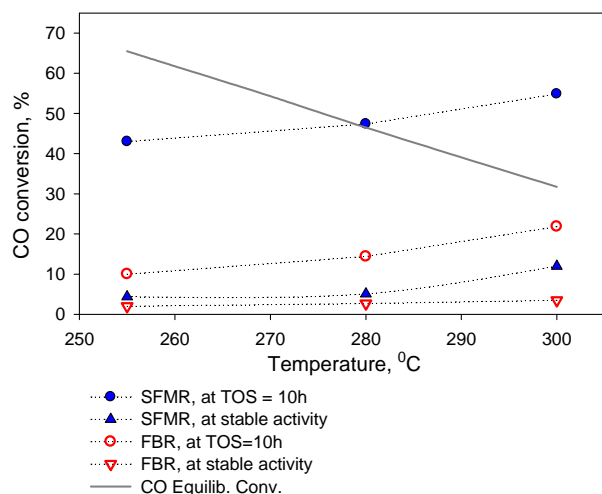


Figure 1: Activity of Pd/CeO₂ as a coating in the SFMR (filled symbols) and as a powder in the FBR (open symbols) after 10 h (circles) and after stabilization (triangles) as a function of reaction temperature. Contact time $W/F = 110$ [ms·gcat/ml] and pressure 80 bar.

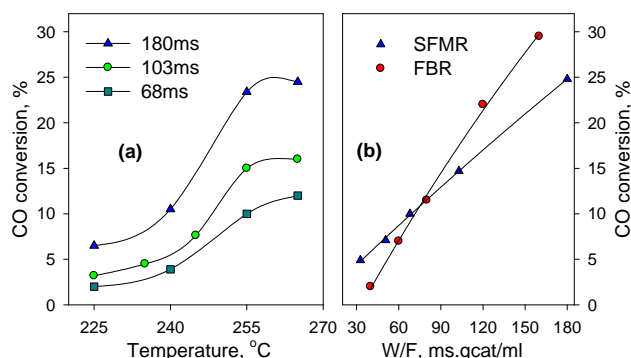


Figure 2: (a) Activity of CuO/ZnO/Al₂O₃ coated foils in SFMR as function of temperature for different contact times (W/F). (b) Comparison of CuO/ZnO/Al₂O₃ based SFMR and FBR experiments at 255 °C and 80 bar as a function of W/F .

The CuO/ZnO/Al₂O₃ coated microchannels have different behavior in the SFMR compared to Pd/CeO₂. The optimum reaction temperature appears to be 250-265°C for the Cu system (Fig. 2a), as for industrial operation. The Cu catalyst slowly deactivated by 20 % over a 300 h period, during which the conditions were varied, and the methane selectivity was always below 10%. Figure 2b shows higher conversion in the SFMR than in the FBR on a CuO/ZnO/Al₂O₃ mass basis for the shortest contact times, while at longer contact time, the highest conversion is obtained in the FBR. Since temperature gradients exist mainly in the FBR, but depend on conversion level and feed flow rate, the reverse reaction may contribute as conversion and residence time increase. Fig. 2b may, however, also reflect very different characteristics of flow and mass transfer.

The liquid product analysis and detailed catalyst characterization is required to better understand the behavior of the catalytic coatings in the SFMR. These are in progress and will be presented to elucidate the reaction data.

Conclusion

A stacked foil microreactor (SFMR) was developed and used to study different catalysts for the methanol synthesis under high pressure (80 bar). The activity of the Pd/CeO₂ SFMR foil coating was significantly better than Pd/CeO₂ particles prepared by deposition-precipitation and applied in the FBR. The same CuO/ZnO/Al₂O₃ coprecipitated catalyst was used in both reactors with an additional step of slurry preparation for coating the SFMR foils. Differences between the two reactor types are found using the Cu catalyst that seems to relate to temperature and possibly to mass transfer characteristics.

Acknowledgements

The Remote Gas project performed under the strategic Norwegian Research program PETROMAKS. The authors acknowledge the partners; StatoilHydro, UOP, Bayerngas Norge, Aker Solutions, DNV, and the Research Council of Norway (168223/S30) for support.

References

- Oezer, N.; Cronin, J. P.; Akyuz, S. Electrochromic Performance of Sol-Gel deposited CeO₂ Films, *SPIE* **1999**, 3788, 103
- Cornthvaite, D. *United States patent* **1975**, 3,923,694
- Phan, X. K.; Bakhtiary, H. D.; Myrstad, R.; Venvik, H. J.; Thormann, J.; Pfeifer, P.; Holmen, A. Preparation and performance of Cu-based monoliths for methanol synthesis. *In preparation*
- Shen, W. J.; Ichihashi, Y.; Okumura, M.; Matsumura, Y. Methanol synthesis from carbon monoxide and hydrogen catalyzed over Pd/CeO₂ prepared by the deposition-precipitation method. *Catalysis Letters* **2000**, 64, 23