

Abschlussbericht für Max-Buchner Stipendium 3607

Antragssteller:

Dr. Gonzalo Prieto
Max Planck Institut für Kohlenforschung
Kaiser Wilhelm Platz, 1 45470
Mülheim a.d. Ruhr

Thema: *Design sowie tomographisch-strukturelle Quantifizierung hierarchisch poröser Katalysatoren für Tandem-Prozesse zur Umsetzung von Synthesegas*

1. Summary of research results.

The Max-Buchner project has focused on the development of hierarchically porous cobalt-based Fischer-Tropsch catalysts uniting a high selectivity toward liquid (C_{5+}) olefin products with a negligible activity for the water-gas-shift reaction, responsible for the production of CO_2 byproduct. The development of automated FIB-SEM tomography routines revealed how different soft- and hard-templating synthesis routes enable the tuning of parameters such as macropore volume, macropore size and connectivity, while preserving a similar mesoporous backbone in the catalysts. Freeze cast methods were additionally developed to assemble meso-macroporous micromonolith catalysts with hybrid Al_2O_3 /carbon nanotube (CNT) backbones. Highly interconnected and trimodally organized porosities, integrating two levels of macroporosity, provided the highest intrapore transport rates, as reflected by a low degree of secondary processing of the olefin primary products under synthesis gas conversion conditions and thus unusually high selectivity to C_3 - C_{10} olefin products. Furthermore, the incorporation of CNTs into the catalyst backbone, served to achieve higher thermal conductivities, inhibiting the development of hotspots within the catalyst structure, and thus preserving the high olefin selectivity in a wider range of temperatures (453-513 K). Selectivities to C_5 - C_{10} olefins up to >30% at CO conversion levels of >20% could be achieved with optimized catalysts, remarkably while keeping CO_2 selectivity <1.5%. The project results realized the single-pass conversion of synthesis gas with high selectivity to liquid olefins an essentially no CO_2 production and open the door to tandem catalytic processes in which the olefinic product fraction is processed *in situ* in a wide range of operation temperatures.

2. List of publications.

1. N. Duyckaerts, M. Bartsch, I.-T. Trotus, N. Pfänder, A. Lorke, F. Schüth, G. Prieto*, *Intermediate product regulation in tandem solid catalysts with multimodal porosity for high-yield synthetic fuel production*, *Angewandte Chemie International Edition* 56 (2017), 11480–11484. DOI: [10.1002/anie.201705714](https://doi.org/10.1002/anie.201705714).
2. J. Kim, V. Nese, J. Joos, K. Jeske, N. Duyckaerts, N. Pfänder, G. Prieto*, *Directional freeze-cast hybrid-backbone meso-macroporous bodies as micromonolith catalysts for gas-to-liquid processes*, *J. Mater. Chem. A* 6 (2018) 21978-21989. (Emerging Investigators 2018 Special Issue). DOI: [10.1039/C8TA07512C](https://doi.org/10.1039/C8TA07512C).
3. T. Rodenas, S. Beeg, I. Spanos, S. Neugebauer, F. Girgsdies, G. Algara-Siller, P. P. M. Schleker, P. Jakes, N. Pfänder, M. Willinger, M. Greiner, G. Prieto, R. Schlögl, S. Heumann, *2D Metal Organic Framework-Graphitic Carbon Nanocomposites as Precursors for High-Performance O₂-Evolution*, *Adv. Energy Mater.* (2018) 8, 1802404. DOI: [10.1002/aenm.201802404](https://doi.org/10.1002/aenm.201802404).
4. Duyckaerts, Nicolas; Jeske, Kai; Schüth, Ferdi; Prieto, Gonzalo*. *Neue Möglichkeiten der Treibstoffproduktion aus unkonventionellen Ausgangsstoffen durch 3D-Bildgebung auf Nanaoskala*, *Max Planck Gesellschaft Jahrbuch 2018*. https://www.mpg.de/11725569/_jb_2018?c=12090594.

3. List of contributions to scientific conferences and workshops.

1. N. Duyckaerts^a, K. Jeske^a, M. Bartsch^b, A. Lorke^b, F. Schüth^a, G. Prieto^{a,*}, *Tandem catalyst design for intensified syngas-to-hydrocarbons technologies*. **Young Chemist Symposium 2017, 12.10.1017, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany**. Type: Poster contribution.
2. N. Duyckaerts^a, K. Jeske^a, M. Bartsch^b, A. Lorke^b, F. Schüth^a, G. Prieto^{a,*}, *Tandem catalyst design for intensified syngas-to-hydrocarbons technologies*. **Max-Planck-Institut für Kohlenforschung Institute seminar, 12.12.2017, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany**. Type: Poster contribution.
3. Kai Jeske^a, Marcos Farpón^a, Burak Atakan^b and Gonzalo Prieto^{a,*}, *Tandem catalysis: strategies to adjust the spatial and thermal intimacies of integrated solid catalysts*. **Max-Planck-Institut für Kohlenforschung Institute seminar, 11.06.2018, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany**. Type: Poster contribution.
4. Kai Jeske,^a Jonglack Kim,^a Valentina Nese,^a Jochen Joos,^b Nicolas Duyckaerts,^a Norbert Pfänder,^c and Gonzalo Prieto^{a,*}, *Olefin-selective Fischer-Tropsch synthesis with Co supported on directional freeze-cast hybrid-backbone meso-macroporous micromonolith bodies*. **52. Jahrestreffen Deutscher Katalytiker, 13-15.03.2019, Weimar, Germany**. Type: Poster contribution.
5. Kai Jeske,^a Jonglack Kim,^a Valentina Nese,^a Jochen Joos,^b Nicolas Duyckaerts,^a Norbert Pfänder,^c and Gonzalo Prieto^{a,*}, *Fischer-Tropsch synthesis on freeze-cast hybrid-backbone meso-macroporous micromonolith catalysts: reconciling high pore transport rates with improved reaction heat management*. **12th Natural Gas Conversion Symposium, 02-06.06.2019, San Antonio, Texas, USA**. Type: Oral contribution.

6. Jonglack Kim^a, Valentina Nese^a, Jochen Joos^b, Ellen Ivers-Tiffée^b, Nicolas Duyckaerts^a, Norbert Pfänder^c, and Gonzalo Prieto^{a,*}; *Hierarchically porous monolithic microstructures as catalysts for intensified syngas-to-liquid processes*. **Young Chemist Symposium 2017, 12.10.2017, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany**. Type: Poster contribution. *Best Poster Prize*.
7. Jonglack Kim^a, Valentina Nese^a, Jochen Joos^b, Ellen Ivers-Tiffée^b, Nicolas Duyckaerts^a, Norbert Pfänder^c, and Gonzalo Prieto^{a,*}; *Hierarchically porous micromonolithic structures with hybrid backbones as catalysts for intensified syngas-to-liquid processes*. **51. Jahrestreffen Deutscher Katalytiker, 14-16.03.2018, Weimar, Germany**. Type: Poster contribution. *Best Poster Prize*.

4. List of patents (applications).

1. F. Schueth, G. Prieto, N. Duyckaerts, *Process for converting synthesis gas to liquid hydrocarbons, device for carrying out the process and catalyst for use therefor*.
WO 2018/162363A1.

5. Major activities and results.

In the course of this 1-year fellowship, we have first developed an automated, unsupervised routine for a Helios Nanolab dual-beam microscope, in cooperation with the Lorke group (CENIDE, Duisburg-Essen University). This routine has enabled automated collection of FIB-SEM data, and thus increased notably the data throughput for tomographic reconstructions of hierarchically porous catalyst materials. (Publications 1-3).

In parallel, various synthesis routes have been explored to introduce various types of macroporosity in Al₂O₃-supported catalysts for the Fischer-Tropsch reaction. Soft-templating routes were based on the combination of non-ionic liquid surfactants and nanosized pseudo-boehmite precursors for Al₂O₃. Hard-templating routes relied on, first, the controlled synthesis of nanometer- and micrometer-sized polymer beads and their subsequent incorporation into synthesis gels containing nanosized pseudo-boehmite precursors for Al₂O₃. Thermal calcination treatments rendered gamma-Al₂O₃ catalyst support materials with mesoporous and macroporous networks. (Publication 1, another publication in preparation).

We have applied FIB-SEM tomography, coupled to quantitative 3D image analysis, to visualize and quantify the internal architecture of high-surface area, multi-modal meso-macroporous RuCo/ γ -Al₂O₃ catalysts for synthesis gas conversion. The spatial resolution offered by FIB-SEM tomography is particularly suitable to image macroporous networks. The 3D reconstruction of the tomograms allowed a precise visualization of the internal macropore

networks in the catalysts, overcoming limitations of alternative Hg intrusion porosimetry methods which probe exclusively unconstrained macropores connected to the outer surface of the particles. Access to the internal structure of the materials made it possible to identify composition ranges for the synthesis gels suitable to prepare catalyst materials with either bi-modal meso-macroporous or tri-modal meso-macro-macroporous structures. In addition, several structural parameters of relevance for molecular diffusion could be quantified by image analysis after tomogram segmentation. The skeleton of the macropore system was computed through a morphology-preserving thinning algorithm. Macropore connectivities were quantified using an algorithm based on the Euler characteristic of the corresponding set of voxels, while a local trabecular thickness algorithm was applied on the set of voxels corresponding to the mesoporous Al_2O_3 phase to quantify the diffusion distances for primary reaction products through the mesoporous network towards the connected macropores (Fig. 1).

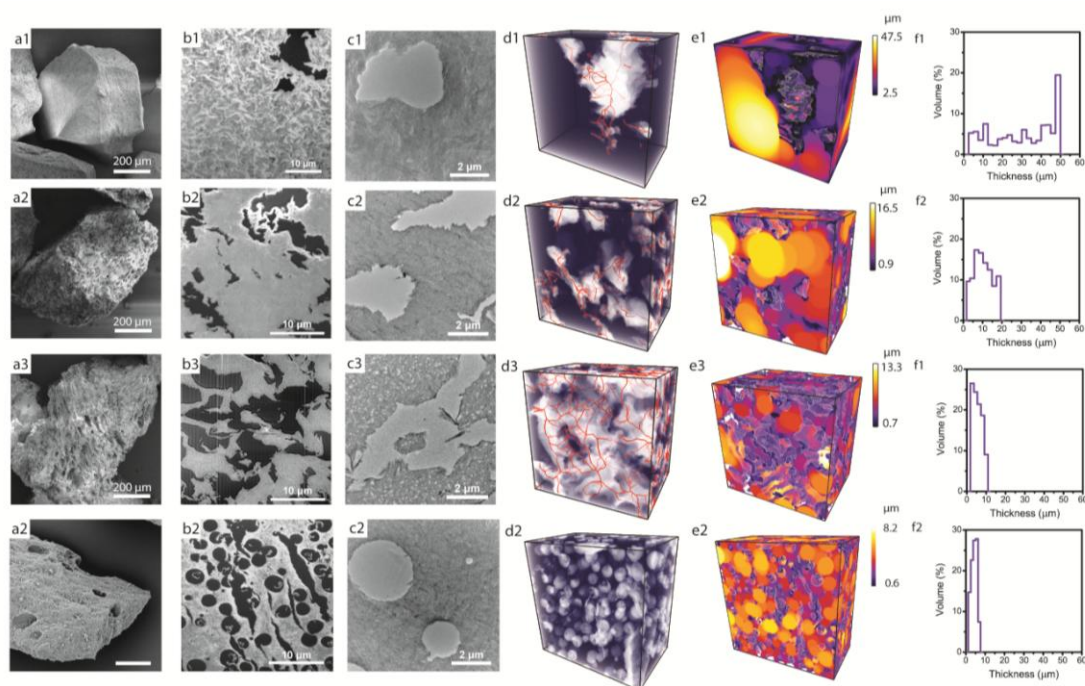


Figure 1: a) SEM micrographs of the outer particle surface, b) cross-sectional SIB-SEM micrographs, c) cross-sectional TEM micrographs, d) reconstructed FIB-SEM tomograms, e) 3D contour maps for the maximum mesopore transport distance to nearest macropore and f) histograms for the maximum mesopore transport distance to nearest macropore for Co-based Fischer-Tropsch catalysts supported on hierarchically porous meso-macroporous gamma- Al_2O_3 carriers. Top three materials obtained through soft-templating methods and bottom material synthesized using a hard-templating approach. (Unpublished results).

Hard-templating approaches based on directional freeze casting of micromonolithic bodies were also explored to synthesize hierarchically porous catalysts for synthesis gas conversion.

Profiting from the high material compatibility of the synthesis method, which is amenable to synthesize not only single-component materials but also bodies with hybrid backbones, catalysts were synthesized with hybrid $\text{Al}_2\text{O}_3/\text{CNT}$ backbones. A honeycomb-shaped and axially oriented macroporous architecture was achieved through the use of zirconium acetate as ice growth modulator. As revealed by X-ray tomography, coupled to quantitative image analysis (Fig. 2) the macrochannel size and wall thickness, but also the extent of axial heterogeneities in macropore diameter and spatial orientation, depended on the axial temperature gradient rate during casting.

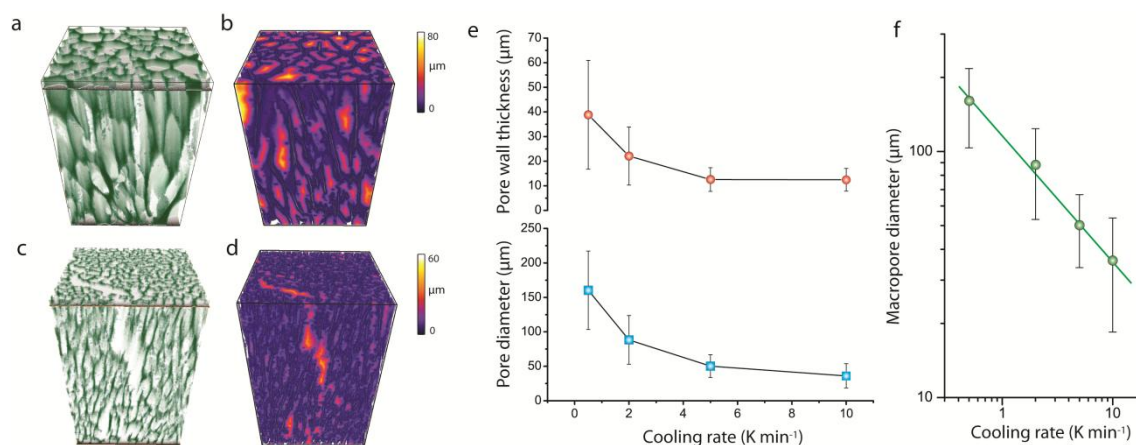


Figure 2: a,c) Surface-rendered 3D reconstructed X-ray tomograms and b,d) local thickness 3D contour maps for the macropore diameter for CNT-ZrAlO_x micromonoliths freeze cast at cooling rates of -0.5 K min⁻¹ (a,b) and -10 K min⁻¹ (c,d). e) Evolution of the volume-averaged macropore diameter and macropore wall thickness with the cooling rate applied to freeze cast CNT-ZrAlO_x micromonoliths. f) Relationship between the volume-averaged macropore diameter and the cooling rate applied during freeze casting for CNT-ZrAlO_x micromonoliths. Error bars correspond to the standard deviation of the average. (Publication 2).

Next, the RuCo/Al₂O₃ catalysts were tested for the Fischer-Tropsch conversion of synthesis gas into synthetic hydrocarbons under industrially relevant reaction conditions. Catalysts synthesized on hierarchically porous alumina carriers afforded a much higher olefin-to-paraffin ratio than those based on conventional, strictly mesoporous supports (Fig. 3). Moreover, research has been performed on promoters to further enhance the selectivity to liquid olefins. Optimal promotion conditions were identified, which resulted in higher olefin-to-paraffin ratios and selectivities to C₅-C₁₀ olefins up to >30% at relevant CO conversion levels of >20%, notably while keeping CO₂ selectivity <1.5% (carbon basis, unpublished results). Hybrid CNT-Al₂O₃ backbone micromonolith catalysts showed also a high selectivity to liquid olefins, owing to the fast evacuation of these primary reaction products from the metal active sites through the directional macropore system. Remarkably, the high olefin selectivity could be maintained up to higher operation temperatures compared to those catalysts based on all-oxide

supports, due to a higher effective thermal conductivity which inhibits the development of hotspots under industrially relevant operation conditions (Publication 2).

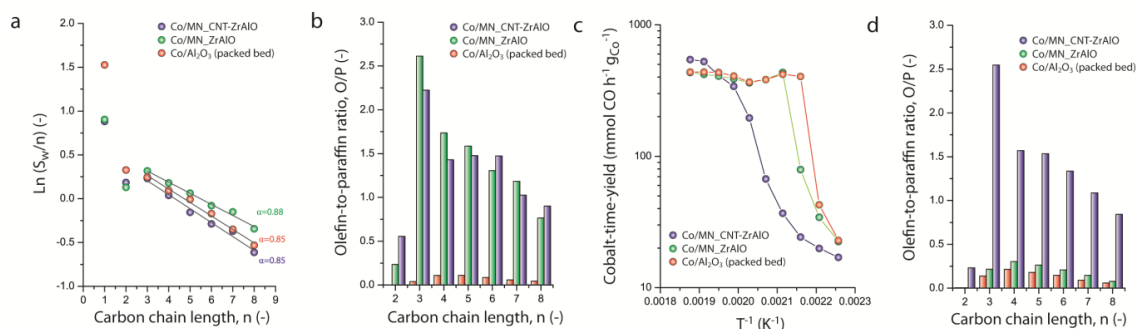


Figure 3. a) Anderson-Schulz-Flory hydrocarbon chain-length distribution plots, and b) olefin-to-paraffin molar ratio for hydrocarbon products in the carbon chain length range from C₂ to C₈, for different Co-based Fischer-Tropsch catalysts at 463 K. c) Evolution of the metal-specific Fischer-Tropsch reaction rate (cobalt-time yield) with the reaction temperature for different Co-based Fischer-Tropsch catalysts. d) Olefin-to-paraffin molar ratio for hydrocarbon products in the carbon chain length range from C₂ to C₈, for different Co-based Fischer-Tropsch catalysts at 483 K. WHSV=1.44 gCO gCo⁻¹ h⁻¹, P=20 bar, H₂/CO=1.0.

The results illustrate how a multipronged catalyst design, integrating the tuning of hierarchical porosities (assisted with 3D imaging and image analysis) and the adjustment of the chemical composition at the active site level, enables the single-pass conversion of synthesis gas with high selectivity to liquid olefins and essentially no CO₂ production (Publications 1 and 4).

6. Collaborations established and potential industrial usage of the results.

In the course of this project, the following scientific cooperations have been established:

1. With the group of Prof. Axel Lorke (CENIDE, Duisburg-Essen University) in the field of FIB-SEM tomography.
2. With the group of Dr. Marco Haumann (Friedrich-Alexander-Universität, Erlangen-Nürnberg), in the field of catalysts in ionic liquids confined to hierarchically porous hosts.
3. With Dr. Joos (KIT, Karlsruhe) in the area of high-resolution X-ray tomography.

The results of the project bear potential technological interest and thus a patent application has been filed (see above, section 4).