

Readme – Dataset to „Structural Investigations of Modified Porous Silica Carrier Materials for Heterogeneous Catalysis”

Purpose of data collection:

In the publication “Structural Investigations of Modified Porous Silica Carrier Materials for Heterogeneous Catalysis” we apply a combination of in-depth physisorption analysis, scanning transmission electron microscopy (STEM)-based tomography and small-angle x-ray scattering (SAXS) to elucidate the mesopore space of commercially available, mesoporous silica particles used in liquid chromatography (LiCrospher Si100®), before and after an etching protocol under basic conditions. We use 4-dimethylaminopyridine (DMAP), covalently immobilized in the mesopores, as organocatalyst to investigate the relationship between pore connectivity, accessibility and the yield in a basic organic reaction, here the acylation of alcohols. The functionalized material was further characterized through Diffusive Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) and elemental analysis (EA) and the reaction yield was determined through high performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC-MS). In particular, the interconnection of the mesopores in the pristine as well as the etched material was visualized and quantified by a 3D reconstruction of the materials by appropriate analysis of the nanotomography data.

Details about materials:

Mesoporous silica particles optimized for liquid chromatography (LiCrospher Si100®, average size 5µm, purchased by MZ-Analysentechnik GmbH) were characterized before and after an etching protocol under basic conditions. The method of functionalization with the organocatalyst DMAP can be found in literature.¹

Details about data acquisition:

Physisorption experiments were performed using an “Autosorb iQ” instrument by Quantachrome Instruments at a temperature of 77 K (nitrogen) or 87 K (argon), the latter achieved with a CryoSync and a CryoTune cryostat. Specific surface areas were determined by the Brunauer-Emmett-Teller method. Pore size distributions were calculated using an NLDFT kernel (Ar at 87 K, zeolites/silica, cylindrical pores, adsorption branch (or equilibrium model for the desorption branch) for argon measurements; N₂ at 77 K on silica, cylindr. pores, adsorption branch (or equilibrium model for the desorption branch) for nitrogen measurements) provided by the Quantochrome software ASiQwin. Measurements were carried out by Raoul D. Brand (Institute of Physical Chemistry, Justus-Liebig-University, Giessen, Germany).

The SAXS/WAXS measurements were conducted using the MOUSE instrument and methods (Methodology Optimization for Ultrafine Structure Exploration) at the Bundesanstalt für Materialforschung und – prüfung (BAM). Here, X-rays were generated from a microfocus X-ray tube, followed by multilayer optics to parallelize and monochromatize the X-ray beams to wavelengths of Cu-K α ($\lambda = 0.154$). Scattered radiation was detected on an in-vacuum Eiger 1M detector (Dectris, Switzerland), the detector was placed at multiple distances between 94 mm to 2492 mm from the sample, with concomitant changes in the collimation. Each dataset, consisting of multiple repetitions, was processed using an extensive data correction scheme implemented in DAWN, that places the intensity on absolute units with traceable values and uncertainties. The resulting data was combined into a single curve spanning a Q-range of 0.02-30 nm⁻¹, using an in-house developed, uncertainty-minimizing method.^{2,3} The measurements were carried out by Brian R. Pauw (Bundesanstalt für

Materialforschung und -Prüfung (BAM), Berlin, Germany). The simulation of the SAXS data was based on an algorithm by Schmidt-Rohr.⁴

For scanning transmission electron microscopy (STEM)-based tomography, the samples were broken up and brought into suspension by mortar grinding with ethanol. The sample suspensions were dropcast onto plasma cleaned continuous carbon tomography grids (quantifoil S160-G2140A). 6.5 nm gold fiducial markers in aqueous suspension were dropcast onto the sample grids. HAADF-STEM tomography was performed on a Themis 300 (Thermo Fisher Scientific) probe corrected (S)TEM at 300 kV with a Fishione +/- 80° single tilt tomography holder. The electron probe, operated with an 8 mrad convergence semi angle and a beam current of 100 pA, was raster scanned with a 10 μ s dwell time over 1024 \times 1024 positions across particles approximately 1 μ m in width, using step sizes between 1.6 and 3.2 nm. Tilt series with 2° increments from -70° to +70° were recorded. The tilt series were aligned with help of the fiducial markers in IMOD.⁵ Volumes were reconstructed by SIRT (Simultaneous Iterative Reconstruction Technique). The reconstruction was refined and segmented by DART (Discrete Algebraic Reconstruction Technique) on the basis of SIRT using the Astra Toolbox.^{6,7} Measurements were carried out by Lucas Brauch (Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany).

The morphological analysis was performed with a workflow as described in previous publications.^{8,9} Histograms were calculated using the local thickness plugin of Fiji, whereas the topological analysis based on the skeletonization approach was performed by the procedure presented by Cheng et al.¹⁰

For quantitative analysis of the reactions using 1-phenylethanol, 100 μ L of the collected aliquot were mixed with 750 μ L methyl tert butyl ether and 10 μ L n hexadecane as an internal standard. The contained solution was analyzed with an Agilent 7890B gas chromatograph coupled with an Agilent 5977B mass spectrometer (Agilent Technologies, Santa Clara, CA). Measurements were carried out by Aline Trommer (Institute of Physical Chemistry, Justus-Liebig-University, Giessen, Germany).

For quantitative analysis of the reactions with α -tocopherol, the collected aliquot was washed with distilled water (1:1) to remove acetate salts byproducts and then quenched in 100 μ L i propanol. The alcohol was separated from the responding acetylated form by HPLC, using a Dionex P680 pump (Dionex, Sunnyvale, CA) combined with an Eurospher II CN column (Knauer GmbH, Berlin, Germany) with a mobile phase consisting of 85% hexane and 15% methyl tert butyl ether at a flowrate of 1 mL min⁻¹ equipped with a Dionex UVD170 UV detector (Dionex, Sunnyvale, CA) at a wavelength of 279 nm. Measurements were carried out by Stefan Bernhardt (Institute of Organic Chemistry, Justus-Liebig-University, Giessen, Germany).

For the characterization of the immobilized organic layer, we performed Diffusive Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements on a Bruker alpha (Bruker Corporation, Billerica, MA) in a range of 400-4000 cm⁻¹ and a resolution of 2 cm⁻¹. Measurements were carried out by Aline Trommer (Institute of Physical Chemistry, Justus-Liebig-University, Giessen, Germany).

For the calculation of the catalyst loadings, we used a literature described procedure based on the nitrogen content.¹ For this purpose, the nitrogen content of the functionalized materials was determined by elemental analysis on a Flash EA-1112 CHN-analyzer (Thermo Scientific, Waltham, MA) coupled with a UMX-2 scale (Mettler Toledo, Columbus, OH). Measurements were carried out by Inna Klein (Institute of Organic Chemistry, Justus-Liebig-University, Giessen, Germany).

Structure of provided data:

Physisorption, SAXS, DRIFT and elemental analysis raw data is divided into multiple .txt files with the file name indicating the respective sample and adsorptive. Raw data of hysteresis scanning experiments are named as such, containing the separated data of all measured segments.

HPLC and GC-MS raw data is given as .pdf files containing the integrated chromatograms with the file name indicating the respective sample, with „pristine“ or „etched“ indicating either DMAP functionalized material and „flow“ or „batch“ indicating the type of catalysis. For the experiments in flow, the file name indicates the flow rate used in mL/min. For the experiments in batch, the filename further indicates the reaction time in minutes.

The results of the STEM-based tomography are given as two .tif stacks containing the individual 2D slices that were processed as described above.

References

- (1) Schulze, J. S., Brand, R. D., Hering, J. G. C., Riegger, L. M., Schreiner, P. R., Smarsly, B. M. DMAP Immobilized on Porous Silica Particles and Monoliths for the Esterification of Phenylethanol in Continuous Flow. *ChemCatChem* **2022**, *14*.
- (2) Pauw, B. R., Smith, A. J., Snow, T., Terrill, N. J., Thünemann, A. F. The modular small-angle X-ray scattering data correction sequence. *J Appl Crystallogr* **2017**, *50*, 1800–1811.
- (3) Wang, Z., Villa Santos, C., Legrand, A., Haase, F., Hara, Y., Kanamori, K., Aoyama, T., Urayama, K., Doherty, C. M., Smales, G. J., Pauw, B. R., Colón, Y. J., Furukawa, S. Multiscale structural control of linked metal-organic polyhedra gel by aging-induced linkage-reorganization. *Chemical science* **2021**, *12*, 12556–12563.
- (4) Schmidt-Rohr, K. Simulation of small-angle scattering curves by numerical Fourier transformation. *J Appl Crystallogr* **2007**, *40*, 16–25.
- (5) Kremer, J. R., Mastronarde, D. N., McIntosh, J. R. Computer visualization of three-dimensional image data using IMOD. *Journal of structural biology* **1996**, *116*, 71–76.
- (6) van Aarle, W., Palenstijn, W. J., Cant, J., Janssens, E., Bleichrodt, F., Dabavolski, A., Beenhouwer, J. de, Joost Batenburg, K., Sijbers, J. Fast and flexible X-ray tomography using the ASTRA toolbox. *Optics express* **2016**, *24*, 25129–25147.
- (7) Batenburg, K. J., Sijbers, J. DART: a practical reconstruction algorithm for discrete tomography. *IEEE transactions on image processing a publication of the IEEE Signal Processing Society* **2011**, *20*, 2542–2553.
- (8) Da Prates Costa, E., Huang, X., Kübel, C., Cheng, X., Schladitz, K., Hofmann, A., Göbel, U., Smarsly, B. M. Tuning Mesopore Accessibility of Ce_{0.18}Zr_{0.64}Y_{0.15}La_{0.03}O_{2-δ} by Hydrothermal Post-treatment—A Case Study for Ceria-Based Oxidation Storage Materials. *Langmuir the ACS journal of surfaces and colloids* **2023**, *39*, 17664–17679.
- (9) Da Prates Costa, E., Huang, X., Kübel, C., Cheng, X., Schladitz, K., Hofmann, A., Göbel, U., Smarsly, B. M. Effects of Hydrothermal Treatment on Mesopore Structure and Connectivity in Doped Ceria-Zirconia Mixed Oxides. *Langmuir the ACS journal of surfaces and colloids* **2023**, *39*, 177–191.
- (10) Cheng, X., Föhrst, S., Redenbach, C., Schladitz, K. Detecting Branching Nodes of Multiply Connected 3D Structures. In *Mathematical Morphology and Its Applications to Signal and Image Processing*; Burgeth, B., Kleefeld, A., Naegel, B., Passat, N., Perret, B., Eds.; Springer International Publishing: Cham, 2019; Vols. 11564, pp. 441–455.