

University of Stuttgart
Germany

SFB Summer School

21.09.-23.09.2020
University of Stuttgart

Abstract
Booklet

Program

	Mo, 21.09.2020	Di, 22.09.2020	Mi, 23.09.2020
9:00 - 9:15		A2	
9:15 - 9:30			
9:30 - 9:45		A7	A3
9:45 - 10:00			
10:00 - 10:15	Hygiene Concept	Ventilation	
10:15 - 10:30			C4
10:30 - 10:45	A1	A5	Ventilation
10:45 - 11:00			
11:00 - 11:15	Ventilation	B3	C3
11:15 - 11:30		Ventilation	
11:30 - 11:45	A6		C5
11:45 - 12:00		Lunch Break	
12:00 - 12:15	A4		Lunch Break
12:15 - 12:30	Ventilation		
12:30 - 12:45			
12:45 - 13:00	B2	C2	
13:00 - 13:15			B1
13:15 - 13:30	Lunch Break	C6	
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14:00 - 14:15	C1	Interviews with Alumni	Glorius
14:15 - 14:30			
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14:45 - 15:00			Ventilation
15:00 - 15:15			
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Monolithic polymeric supports with uniform diameter pores for continuous catalytic reactions

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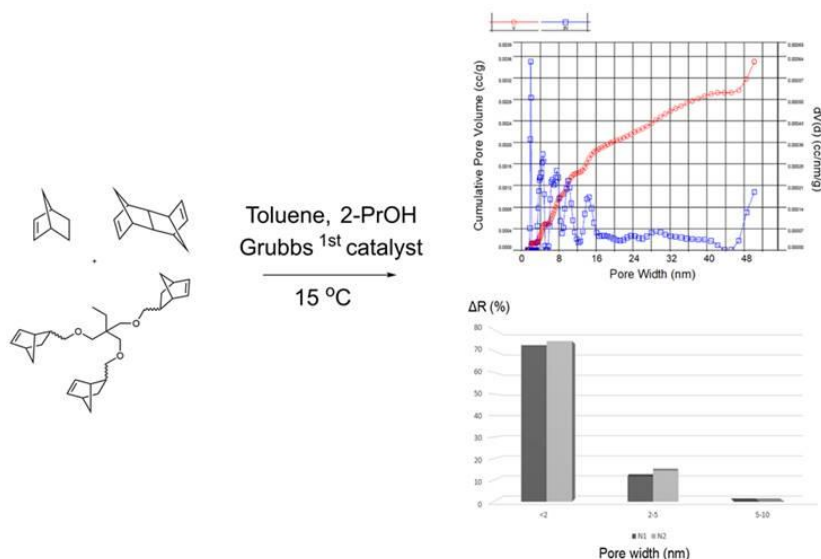


Figure 1: Synthesis of mesoporous ROMP-derived, poly(norborn-2-ene)-based monolithic supports with defined, unimodal mesoporosity in the range of 1-10 nm with flow-through pores in the micrometer range.

In the area of molecular heterogeneous catalysis, catalysts must be located at the surface of the structure-forming microglobules to be accessible for reactants. Given the dimensions of typical organometallic catalysts (ca. 1.5 nm), the choice of a mesoporous material (< 50 nm) raises the possibility that selective binding of a catalyst inside the mesopores of the support material provides sufficient levels of confinement to generate confined conditions during the continuous catalytic reactions. [1-2] The synthesis of a monolithic support is conveniently accomplished by solvent-induced phase separation (SIPS), which follows the Flory-Huggins theory. [3-4] Within the confines of choice in a one-step procedure, the use of appropriate amounts of monomer(s), crosslinker(s) and porogenic solvents offers access to design the polymeric monolithic support with defined, unimodal mesoporosity in the range of 1-10 nm with the flow-through porosity in the micrometer range that allows for fast mass transfer. The living nature of the ROMP-based polymerization allows for the synthesis of well-defined monoliths which are easily post-functionalized. [5]

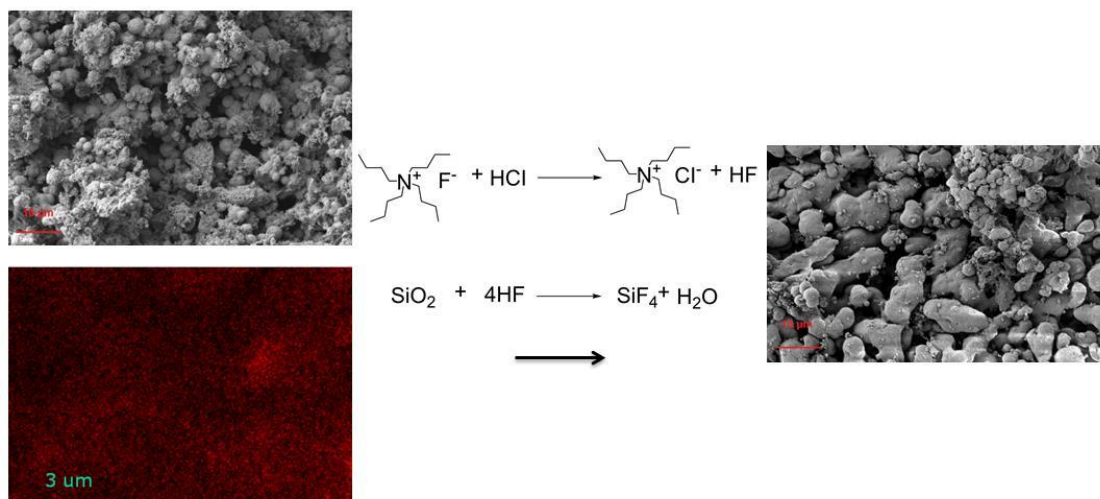


Figure 1: Hard templating on the ROMP-derived, poly(norborn-2-ene)-based monolithic structure.

In course of our activities in the area of molecular heterogeneous catalysis in confined geometries, ROMP-derived, poly(norborn-2-ene)-based monolithic supports with tailored mesoporosity that fulfill the general requirements for polymeric monoliths such as dimensional stability, unitary structure, incompressibility, tailored mesoporosity, transport pores in the micrometer range, high linear flow (> 2 mm/s) at low back pressure (< 2 bar) have successfully been prepared under solvent-induced phase separation conditions. Currently, we pursue a systematic study of the influence of size and properties of tailored inorganic nanowires (SiO_2 ($d \times l$: 10 nm \times 200 nm)) used in a hard templating process on the size, size distribution, and morphology of the pores in the formed monoliths. Applications in catalysis under confined geometries will be outlined.

- [1] G. Y. Yang, N. Tsubaki, J. Shamoto, Y. Yoneyama, Y. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8129-8136.
- [2] J. Yuan, A. M. Fracaroli, W. G. Klemperer, *Organometallics*. **2016**, *35*, 2149-2155.
- [3] P. J. Flory, *J. Chem. Phys.* **1942**, *10*, 51-61.
- [4] P. J. Flory, *J. Chem. Phys.* **1949**, *17*, 223-240.
- [5] S. Lubbad, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2003**, *24*, 580-584.

Tunable Block Copolymer Templates for Spatially Controlled Immobilization of Molecular Catalysts and Redox Probes

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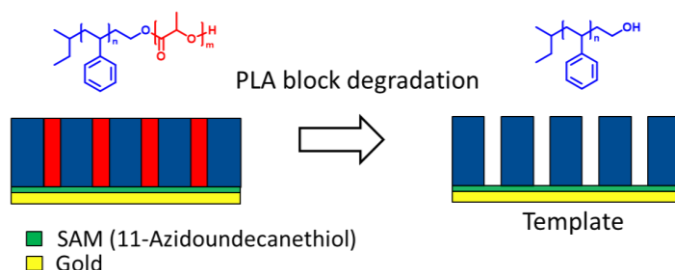


Figure 1: Sketches of a cylindrical PS-*b*-PLA block copolymer thin film on a SAM treated gold substrate in side view and minority block degradation of PLA resulting in a mesoporous template

In this project, we are aiming to prepare mesoporous thin film templates from polystyrene-*block*-poly lactide (PS-*b*-PLA) block copolymer (BCP) films on gold substrates in order to study molecular heterogeneous catalysis and electrochemistry in confinement. To create such thin film templates, we use BCP solvent vapor (SVA) controlled self-assembly. The soft-etchable poly lactide (PLA) minority block gets then hydrolyzed to result in a highly ordered porous thin film template. Using cross-sections of these films we prove continuous pores to the substrate by techniques such as scanning electron microscopy.

The project involves tailor-made synthesis of the PS-*b*-PLA block copolymers. Well-defined systems have been synthesized using living anionic polymerization of hydroxyl functionalized PS followed by the ring-opening polymerization (ROP) of D,L-lactide. First experiments on PS-*b*-PLA linear polymers resulted in templates of cylindrical features with domain spacings of around 22 nm and pore sizes around 12 nm. Since smaller pore diameters are required for the desired confinement effect, we have also focused on different molecular PS-*b*-(PLA)₃ miktoarm architectures. Changing to a more branched BCP architecture can produce templates with domain spacings smaller than 20 nm [1].

Because molecular heterogeneous catalysis is usually performed in organic solvents, a solvent stable template matrix is needed. Therefore, vinyltriphenylamine (VTPA) is co-polymerized with styrene in the first matrix block. These TPA units can undergo irreversible electrochemical crosslinking in polymer films. [2]

To enable the possibility of functionalization on the pore bottom, gold substrates are modified with 11-azidoundecanethiol based self-assembled monolayers (SAM). Via “Click”-chemistry different molecular probes such as alkyne ferrocene or heterogeneous catalysts can be successfully immobilized. Template functionalization is characterized using X-ray Photoelectron Spectroscopy (XPS) and Infrared Reflectance Absorbance Spectroscopy (IRRAS). Further the electrochemical behavior of the immobilized redox probes is investigated using scan-rate dependent cyclic voltammetry (CV) [3]. In this way it is possible to study the diffusion of redox-active units within the etched mesoporous templates.

[1] L. Stein, P. Dreier, K. Dirnberger, H. Frey, S. Ludwigs, in prep. (2020).

[2] P. Blanchard, C. Malacrida, C. Cabanetos, J. Roncali, S. Ludwigs, *Polymer International* 68, 589, (2019).

[3] S.S.Y. Lu, S. Ludwigs, *Macromol. Rapid Comm.*, 41, 1900485, (2020).

Molecular Heterogeneous Catalysis in Confined Geometries Real Structure and Functionalization of Covalent Organic Frameworks

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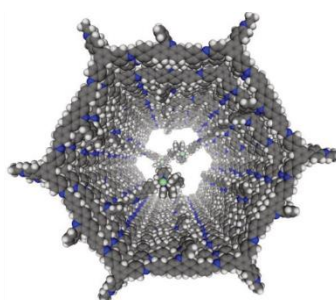


Figure 1: Covalent organic framework.

Covalent organic frameworks (COFs) are 2D or 3D polymers consisting entirely of light elements and are defined by three features: covalent connectivity, porosity, and crystallinity.^[1] Most COFs are synthesized under solvothermal conditions by reversible-bond-forming reactions. Reversibility of the COF linkage is key to obtain well-defined local and long-range structures by error correction and defect healing.^[2] Covalently-bonded 2D COF sheets build up 3D structures via van-der-Waals and other non-covalent interactions in the third dimension. This sheet stacking creates structural mesoporosity with well-defined pore sizes and geometries.^[3]

Here we present insights into real-structure COF pore geometries by investigating stacking disorder in a COF. Using total scattering methods and stacking fault simulations, we investigate previously predicted random local layer offsets, which are typically disguised by the apparent crystallographic symmetry. Furthermore, we explore alternative post-modification of imine linked COFs for improved stability against hydrolysis and activation for additional pore-wall functionalization strategies associated to the linkage. Moreover, we present hydroxyl functionalized isorecticular COFs with varying pore sizes as a platform to study confinement effects during catalysis. Successful immobilization of ruthenium-based olefin-metathesis catalysts enables the investigation of confinement effects on ring-closing metathesis.

- [1] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* 2005, 310, 1166-70.
- [2] F. Haase, E. Troschke, G. Savasci, T. Banerjee, V. Duppel, S. Dörfler, M. M. J. Grundei, A. M. Burow, C. Ochsenfeld, S. Kaskel, et al., *Nat. Commun.* 2018, 9, 1-10.
- [3] F. Haase, K. Gottschling, L. Stegbauer, L. S. Germann, R. Gutzler, V. Duppel, V. S. Vyas, K. Kern, R. E. Dinnebier, B. V. Lotsch, *Mater. Chem. Front.* 2017, 1, 1354-1361.

Controlled Synthesis and Functionalization of Mesoporous Silica Materials

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True liquid crystal templating is used to produce mesoporous silica materials (MSMs) with various pore diameters. Direct transfer of the lyotropic liquid crystal structure results in materials with nearly perfect Gaussian pore width distributions (see Fig. 1a). Targeting pore widths down to 3 nm allows the use of standard surfactants such as cetyldimethyl ethylammonium bromide (CDEAB) instead of polymeric amphiphiles, which promises a reduced pore width distribution. Various surfactants and concentrations are tested to analyze the impact on the MSM's structures.

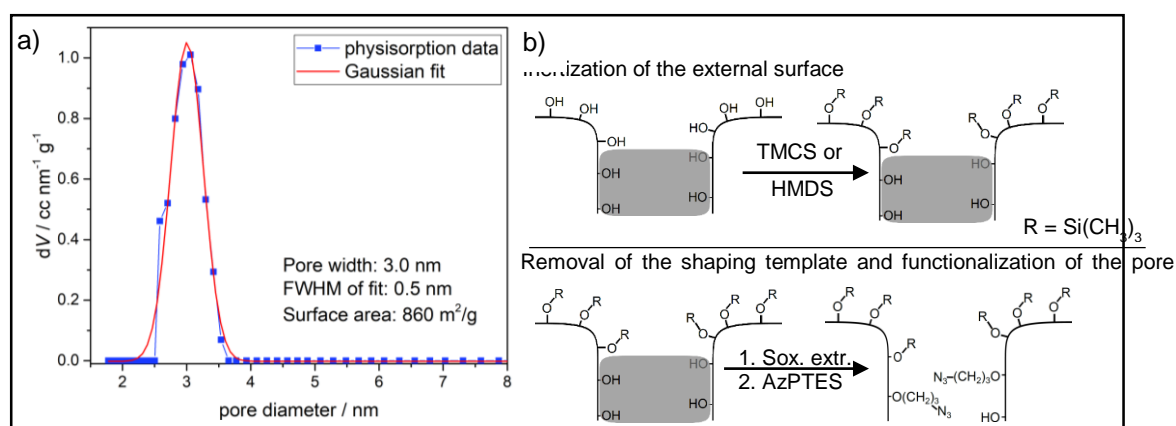


Figure 1: a) Pore width distribution of an MSM produced by true liquid crystal templating from a CDEAB/H₂O system. b) Scheme of the modification process of MSMs.

In order to use the produced MSMs as support material for organometallic catalysts, the controlled functionalization of the external and especially of the internal surface is necessary. One way to modify the MSMs for the attachment of the organometallic catalysts is, in a first step, the inertization of the external surface with a silane. The side groups of the silane used must not show any activity towards the further functionalization steps. After the inertization of the external surface, the template plugging the pores is removed by Soxhlet extraction. Afterwards, the pore walls are modified with a silane which holds a reactive side group to which the organometallic catalyst can be attached in the next step (see Fig. 1b).

A method is developed to ensure that the external surface is completely functionalized which means that the side group connecting the organometallic catalyst to the pore wall can only be located in the mesopores. Furthermore, various conditions of the functionalization step and the adjustment of the concentration of the reactive group on the pore walls are investigated. Additionally, a new method is tested to extract the pore widths of various materials from small angle X-ray scattering by calculation of their electron density maps.

Organic-inorganic hybrid materials with tunable pore size as catalyst supports

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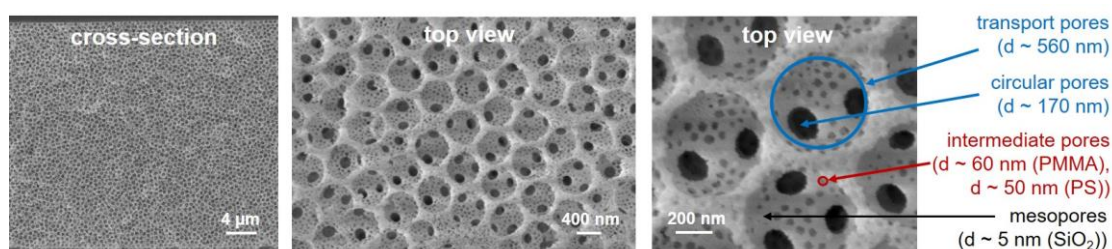


Figure 1: Cross-section and top view SEM images of bimodal silica inverse opal with a hierarchical structure including big transport and circular pores, intermediate pores and mesopores.

The goal of our project is to develop a template-based process for the formation of structured mesoporous organic-inorganic (hybrid) or pure inorganic catalyst supports with tunable pore diameter in the range of 5-20 nm. A bio-inspired method is employed for the synthesis of mesoporous hybrids, where polymer templates such as monoliths (project A1), block copolymers (project A2) and polymer foams [1] (project A7) will be selectively mineralized with oxides like ZnO, TiO₂, SiO₂, ZrO₂ and Al₂O₃ to adjust the pore size. Alternatively, inorganic mesoporous supports as inverse replica of polymer foams and colloidal crystals (project A7) with different pore geometries will be prepared. The surface properties of the deposited inorganic layers shall be manipulated by varying the oxide type and/or by surface functionalization with self-assembled monolayers (SAMs). Then, catalyst molecules (projects B2 and B3) will be selectively attached to the pore surface using “click” chemistry. The impact of the confined space by means of pore size, polarity and shape on: a) the mineralization mechanism, morphology and structure of the deposited oxides and b) the catalytic reactions (B2, B3) (activity and reactant transport (C5)) shall be studied.

Here, we present the synthesis of hierarchically structured ZnO and TiO₂ inverse opals (Figure 1) applying different assembly techniques. The influence of various experimental variables such as the oxide precursor, diameter of the polystyrene colloidal crystals and the hydrolyzing agent on the morphology of the resultant inverse replica was studied [2]. Additionally, the SAM formation on thin oxide films and mineralization of mesoporous polymer templates is discussed.

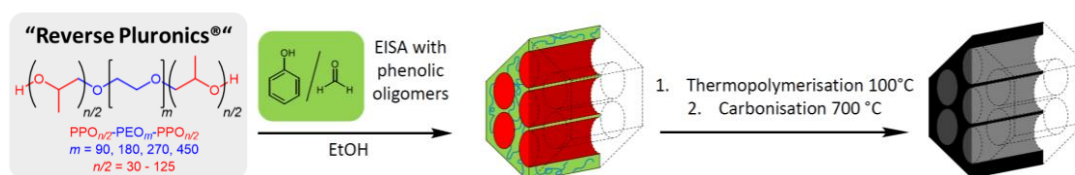
- [1] Y. Qawasmi, P. Atanasova, L. Grassberger, T. Jahnke, Z. Burghard, R. Strey, J. Bill, T. Sottmann, *Colloid Polym. Sci.* 2018, 296, 1805.
- [2] K.R. Phillips, T. Shirman, M. Aizenberg, G.T. England, N. Vogel, J. Aizenberg, *J. Mater. Chem. C*, 2020, 8 (1), 109-116.

Mesoporous Carbons with Controlled Pore Diameter by Block Copolyether Design

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Carbon Materials via soft templating approach.

Reverse “Pluronic”-type polyethers ($\text{PPO}_{n/2}\text{-PEO}_m\text{-PPO}_{n/2}$)[1-3] are employed as structure-directing agents (SDAs) in a modification of a well-established organic soft-templating approach.[4-5] The nanostructure is generated by organization of the block copolyethers in EtOH alongside oligomerized phenolic resins (= carbon precursor) in an evaporation-induced self-assembly (EISA) process. Subsequent cross-linking (100 °C) and carbonization (700 °C) delivers mesoporous carbon materials with controlled porosity and pore diameter distribution. Contrary to what is frequently cited in literature, *Reverse Plurionics* are excellently suited for templating highly ordered carbon materials; moreover, by fine-tuning their architecture (molar mass, relative ration of hydrophilic and lipophilic blocks), we were able to rationally predetermine the pore diameter of the resulting, hexagonally ordered carbons: a continuous spectrum in the range of 5-15 nm can be accessed by adapting the hydrophilic (PEO/PEG, $m = 180\text{-}800$) und lipophilic (PPO, $n/2 = 30\text{-}125$) moieties.[6] The precisely controlled polyethers ($\bar{D}_M < 1.03$) are sourced from a metal- and solvent-free, organocatalyzed polymerization process.[1-2]

Crucially, this enables the preparation of mesoporous carbons in practicable amounts (> 1 g) without the need for manipulating process conditions. The single adaptable parameter is copolyether composition.

- [1] S. Naumann, A. W. Thomas, A. P. Dove, *Angew. Chem. Int. Ed.* **2015**, *54*, 9550-9554; *Angew. Chem.* **2015**, *127*, 9686-9690.
- [2] A. Balint, M. Papendick, M. Clauss, C. Müller, F. Giesselmann, S. Naumann, *Chem. Commun.* **2018**.
- [3] M. Felix, J. R. Bruckner, S. Naumann, *Macromol. Chem. Phys.* **2020**, 1900437.
- [4] F. Zhang, Y. Meng, D. Gu, Y. Yan, C. Yu, B. Tu, D. Zhao, *J. Am. Chem. Soc.* **2005**, *127*, 13508-13509.
- [5] C. Liang, S. Dai, *J. Am. Chem. Soc.* **2006**, *128*, 5316-5317.
- [6] M. Felix, C. Vogler, J. R. Bruckner, S. Naumann (*manuscript in preparation*).

Nano-porous foams and ZnO inverse opals obtained from polystyrene nanoparticles with adjustable size and polydispersity

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Polymer particles have attracted considerable attention due to the possibility of applying inexpensive methods to prepare highly ordered porous materials where the nanoparticle size and polydispersity are crucial for the final pore size and morphology. In this study, we investigated the influence of the sodium dodecyl sulfate (SDS) concentration utilized in the emulsion polymerization on both the properties of the obtained polystyrene (PS) nanoparticles and the morphology of the closed-packed arrangements formed by these particles. Combining dynamic light scattering (DLS), small angle neutron scattering (SANS) and scanning electron microscopy (SEM) we found a strong decrease of the particle radius with increasing SDS concentration which levels off at the same concentration where the polydispersity increases suddenly. Studying the interfacial tension between aqueous SDS solutions and styrene allowed us to link this increase to competing nucleation and growth mechanisms occurring at concentrations above the critical micelle concentration (CMC). The closed packed PS nanoparticles obtained via controlled drying (Fig. 1 middle) were investigated by small angle X-ray (SAXS) and SEM. Both techniques show that the increase in particle polydispersity induces a loss in packing order, while the quantitative SAXS analysis confirmed that polydisperse particles allow a more densely packing. Subsequently, these templates were used for the preparation of novel mesoporous polystyrene and ZnO inverse opals. The former was obtained using an optimized nanofoams by continuity inversion of dispersion (NF-CID) Hier den Text eingeben^[1] procedure yielding in a highly porous material with a bimodal structure consisting of μm -sized large spherical pores surrounded by mesopores of open-cellular morphology (Fig. 1, left). ZnO inverse opals were obtained via the chemical bath deposition (CBD)^[2] method, followed by a pyrolysis step to obtain the inverse replica of the closed-packed PS nanoparticle arrangement (Fig. 1, right). Preliminary studies showed that complete infiltration becomes increasingly difficult when either the size of the PS particles is decreased, or their polydispersity is increased leading to a more densely packing of the particles. In order to improve the diffusion properties of the assembled particles, transport pores will be introduced by assembling crosslinked and non-crosslinked particles, followed by removal of the non-crosslinked particles by an appropriate solvent.

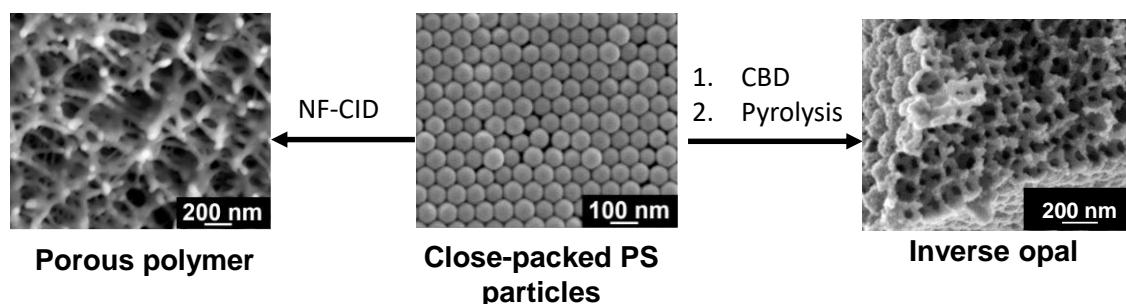


Figure 1: Controlled drying of a dispersions of polymer nanoparticles results in a closed-packed arrangement of the nanoparticles (middle) which can be utilized to produce porous polymers following the NF-CID principle (left) or ZnO inverse opals via the CBD method (right).

[1] R. Strey, A. Müller, DE102010053064A1.

[2] P. Atanasova, N. Stitz, S. Sanctis, J. H. M. Maurer, R. C. Hoffmann, S. Eiben, H. Jeske, J. J. Schneider, J. Bill, *Langmuir : the ACS journal of surfaces and colloids* 2015, 31, 3897.

Tetraaza-Ruthenium-Complexes supported on Azide-Modified SBA-15 Material for the Directed Hydrogen-Autotransfer Catalysis

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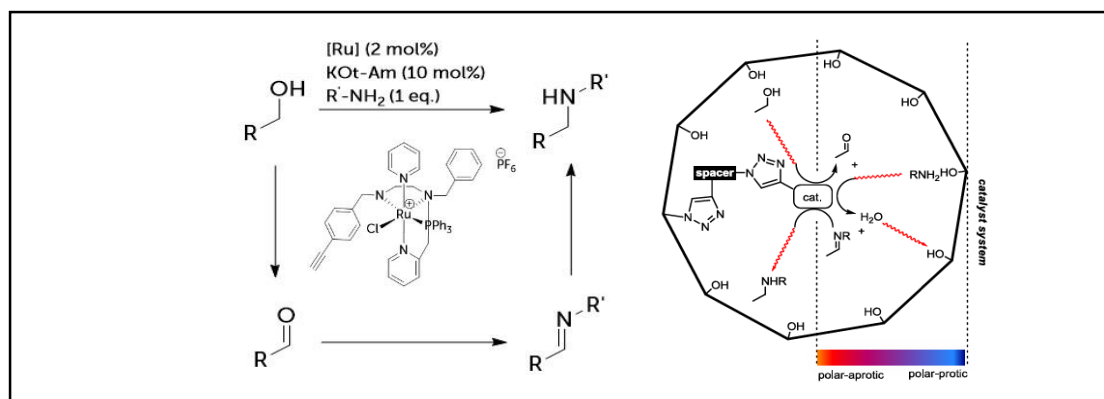


Figure 1: Reaction cascade of the H₂-Autotransfer Catalysis with the for click chemistry modified Ru-Complex (left) and the scheme of the pore with immobilized complex-linker moiety.

The Plietker Group is focusing on the hydrogen-autotransfer catalysis with our tetraaza-ruthenium-complexes^[1]. With the insertion of an alkyne into the ligand the complexes can be easily connected to the materials via click-chemistry. At the moment the azide-SBA-15 material, which is mesoporous, is our material of choice. The synthesis of this kind of materials has been published, among other things, by T. D. Stack in 2012.^[2] By de-functionalization of the outer surface of the as synthesized and the refilled material via Staudinger reduction, the exclusively immobilization of the complex to the inner pore surface can be investigated. Moreover, the influence of the pore entries in contrast to the inner-pore surface can be studied. The next step, the insertion of the spacer molecule leads to a modification of the spacer synthesis to ensure the stepwise coupling with firstly the complex and secondly the material.

[1] D. Weickmann, W. Frey, B. Plietker, *Chem. Eur. J.* 2013, 19, 2741-2748; D. Weickmann, B. Plietker, *ChemCatChem* 2013, 5, 2170-2173.

[2] J. Nakazawa, B. J. Smith, T. Daniel P. Stack, *JACS.* 2012, 134, 5, 2750-2759.

Cationic Molybdenum Imido Alkylidene *N*-Heterocyclic Carbene Catalysts in Confined Geometries For Use in Selective Macrocyclization

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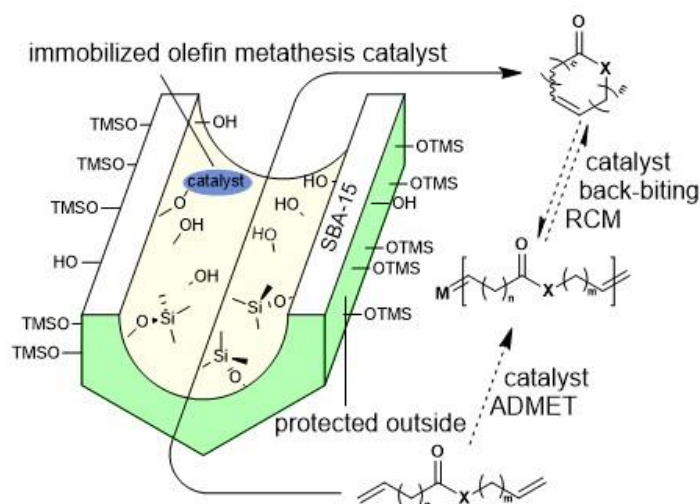
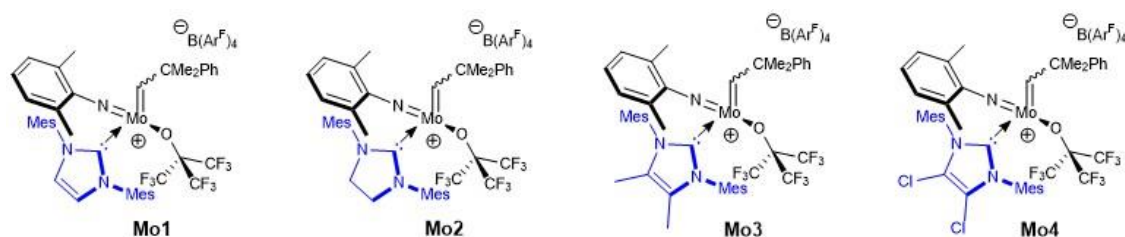


Figure 1: Concept for the synthesis of a variety of macrocycles with a Mo-alkylidene catalyst immobilized in mesoporous materials with defined pore diameter.

Ring closing metathesis (RCM) of long chain dienes provides access to valuable macrocycles. However, state of the art methods require high dilution (1 mM), fairly high catalyst:substrate ratios (1:4-100), static vacuum and suffer from the formation of oligomerization products by competing acyclic diene metathesis (ADMET) polymerization.[1] One approach to improve macrocyclization yields is the exploitation of the back biting reaction in combination with a tailored distillation apparatus[2] or the use of an *N,N*-chelated Ru-alkylidene catalyst.[3] We showed that the immobilization of a 2nd-generation Grubbs-Hoveyda olefin metathesis catalyst in a confined space (SBA-15 with different pore sizes) results in the suppression of ADMET and allows higher substrate concentrations.[4]

Furthermore, it was possible to extend the concept to other catalytic systems *via* the immobilization of cationic Mo-alkylidene-imido-NHC-monoalkoxide complexes.



catalyst@SBA15	MMC/O (conversion [%])	catalyst@SBA15	MMC/O (conversion [%])
Mo1@SBA15 _{50A}	3.3 (17)	Mo3@SBA15 _{50A}	3.4 (23)
Mo1@SBA15 _{62A}	2.5 (42)	Mo3@SBA15 _{62A}	2.5 (42)
Mo2@SBA15 _{50A}	3.5 (29)	Mo4@SBA15 _{50A}	3.3 (23)
Mo2@SBA15 _{62A}	2.6 (28)	Mo4@SBA15 _{62A}	2.4 (26)

Figure 2: Application of the different types of silica containing the catalyst in the macrocyclization of substrates C₁₁₋₅₋₁₁. Ratio of macrocycle formation MMC to the competitive formation of oligomers with different SBA-15.

- [1] *Selected reviews on macrocyclization by olefin metathesis catalysts:* a) M. E. Maier, *Angew. Chem. Int. Ed.* **2000**, *39*, 2073-2077; b) A. Deiters, S. F. Martin, *Chem. Rev.* **2004**, *104*, 2199-2238; c) V. M. Marx, M. B. Herbert, B. K. Keitz, R. H. Grubbs, *JACS* **2013**, *135*, 94-97; d) H. Zhang, E. C. Yu, S. Torker, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2014**, *136*, 16493-16496 e) X. Shen, T. T. Nguyen, M. J. Koh, D. Xu, A. W. H. Speed, R. R. Schrock, A. H. Hoveyda, *Nature* **2017**, *541*, 380-385;
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- [3] C. S. Hgiman, D. L. Nascimento, B. J. Ireland, S. Audörsch, G. A. Bailey, R. McDonald, D. E. Fogg *J. Am. Chem. Soc.* **2018**, *140*, 1604-1607.
- [4] F. Ziegler, J. Teske, I. Elser, M. Dyballa, W. Frey, H. Kraus, N. Hansen, J. Rybka, U. Tallarek, M. R. Buchmeiser *J. Am. Chem. Soc.* **2019**, *141*, 19014-19022.

Chiral Diene Ligands and their Immobilization on Mesoporous Materials for Rhodium Catalysis

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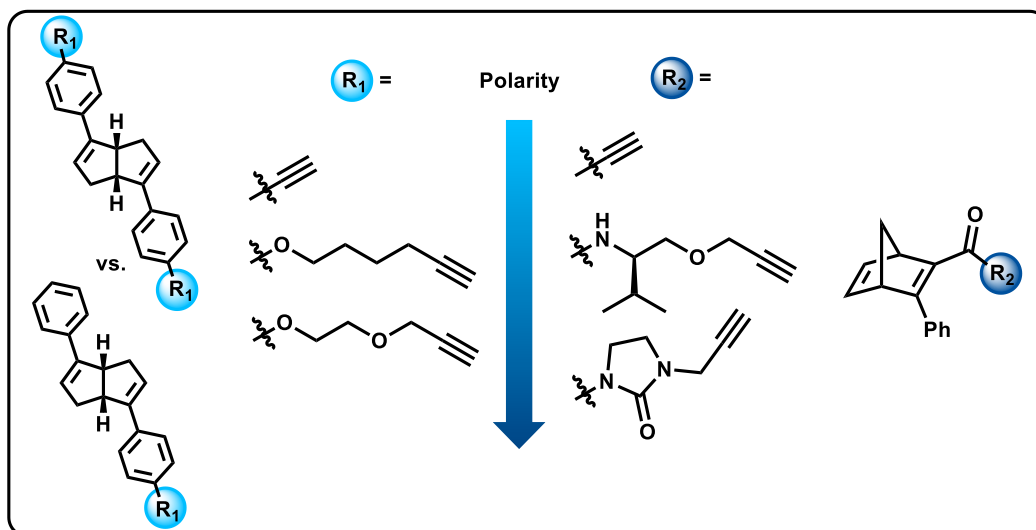


Figure 1: Tetrahydropentalenes (left) and norbornadienes (right) with various spacers of different polarities and lengths.

Several tetrahydropentalene- and norbornadiene-based alkyne-functionalized ligands with spacers of different length and polarity have been successfully synthesized. In a series of immobilization experiments both systems were clicked with various azide-functionalized materials (A2, A4, A5) through copper-catalyzed azide-alkyne cycloaddition (CuAAC). Subsequently, all functionalized materials were applied in the rhodium-catalyzed 1,2-addition of triphenylboroxine to a *N*-tosylimine.

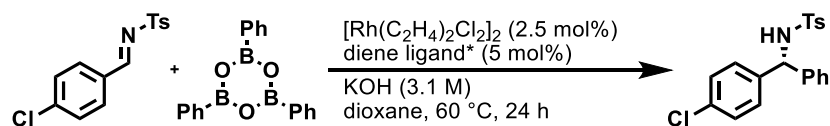


Figure 2: 1,2-Addition of triphenylboroxine to a *N*-tosylimine.

Tetrahydropentalenes with two kinds of substitution patterns were compared: Asymmetric mono- and symmetric double-functionalized dienes. The double-functionalized dienes showed low yields and enantiomeric excesses in the 1,2-addition. In contrast to this, much higher yields and enantioselectivities were achieved for mono-functionalized dienes. For one derivative even higher enantioselectivities were determined than for the corresponding alkyne under homogeneous conditions (figure 1, left).

For the norbornadiene with no spacer between the alkyne and the diene core only low yields were achieved in the 1,2-addition. However, the determined enantiomeric excess of the *N*-tosylamine suggests that the chiral diene is involved in catalysis. It was assumed that a triazole close to the diene system is unfavorable due to possible coordination effects or steric hindrance. Further experiments with spacers between the alkyne and the diene system are pending (figure 1, right).

Solid State NMR

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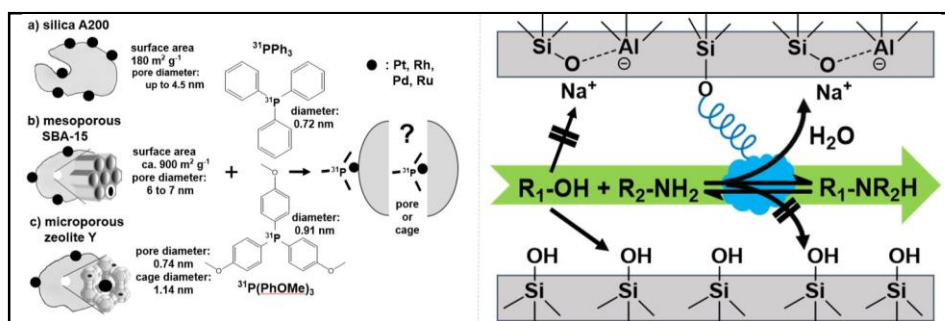


Figure 1: Part 1 (left): Comparison of triphenylphosphine (PPh₃, size=0.72 nm) and tris(4-methoxyphenyl)phosphine (P(PhOMe)₃, size=0.91 nm), on noble metal loaded silica, SBA-15 and zeolite Y. Part 2 (right): Changes of surface adsorption properties for water and alcohol by aluminum modification.

PART 1: Phosphines ($^{31}\text{PR}_3$) with different groups R (phenyl, 4-methoxyphenyl) are demonstrated to be useful molecular probes for quantitatively characterizing the spatial distribution of noble metal (NM) atoms on mesoporous and microporous support materials, such as silica A200, mesoporous SBA-15, and zeolite Y. Complexation of triphenylphosphine (PPh₃) and tris(4-methoxyphenyl)phosphine, P(PhOMe)₃, with Pt, Rh, Pd, and Ru on open surfaces and in mesopores leads to characteristic ^{31}P MAS NMR signals at $\delta = 33$ to 41 ppm. Because of the different molecular diameters of PPh₃ (0.72 nm) and P(PhOMe)₃ (0.91 nm), adsorption of these two probe molecules allows for distinguishing between noble metal atoms located at the outer surface of zeolite particles and those in secondary mesopores and in supercages of zeolites Y. The latter location of noble metal species in zeolite Y is interesting for shape-selective heterogeneous catalysis. For the present work, the high NMR sensitivity of ^{31}P nuclei (spin $I = 1/2$, abundance of 100%) and the characteristic chemical shifts of phosphine complexes formed at Pt, Rh, Pd, and Ru species were utilized. Before the solid-state NMR studies, the reduced noble metal-containing catalysts were physically mixed with the solid phosphines and heated under well-defined conditions. For the first time this method enables the characterization of noble metals nanoparticles directly, using probe molecules and ^{31}P MAS NMR spectroscopy.

PART 2: Alcohol-amine hydrogen-autotransfer reaction is one of the most important methods to prepare nitrogen containing compounds. In this equilibrium reaction, water is a by-product and therefore, removing water from the active sites in molecular heterogeneous catalyst can lead to higher product yields. Thus, we adjust the surface affinity of mesoporous materials for model substrates. The modification with aluminum is a useful approach to change surface polarity of siliceous porous material. In our research, adsorption and desorption of water and methanol as model compounds for alcohols on different porous silicates and aluminosilicates have been investigated by ^1H , ^{23}Na and ^{27}Al MAS NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). At 373 K, microporous and mesoporous materials (Na-ZSM-5 and Na-[Al]SBA-15) display a contrary affinity to water and methanol. The ^{23}Na and ^{27}Al MAS NMR prove different adsorption sites in Na-ZSM-5 and Na-[Al]SBA-15, corresponding with the desorption enthalpies derived from TGA-DSC measurement. We show that Na-[Al]SBA-15 prefers water by a factor 3 over methanol. The preferred water over methanol adsorption is transferable to other mesoporous materials.

Functionalization of a $\text{dppfFe}(\text{CO})_3$ complex to make it clickable – Tetrazine ligand for clicking

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A probe complex was functionalized in a way that it now is possible for it to be fixed onto a surface or into a pore to understand the effects on its electric and geometric structure.

Here a derivative with the dimethylamine functionalization was chosen because this functionality allows the simple addition of clickable benzyl-bromides that paves the way for immobilization and comparison of the different environments.

Both the neutral and the oxidized $\text{dppfFe}(\text{CO})_3$ [1], have been thoroughly studied [2], as well as the here in reported clickable $\text{dppfFe}(\text{CO})_3$, a comparison with an immobilized derivative is now possible.

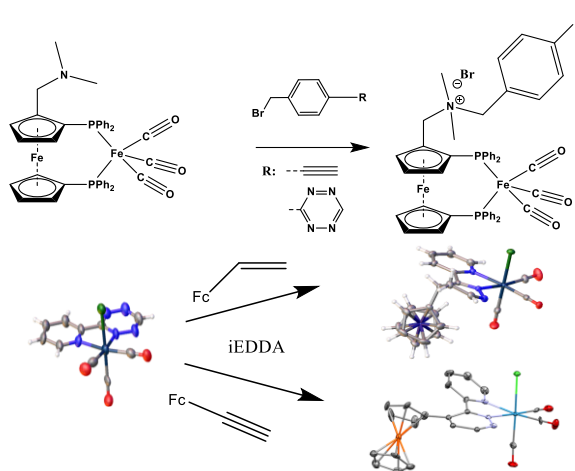


Figure 1: *left:* Addition of clickable benzyl-bromides to dimethylamine functionalization $\text{dppfFe}(\text{CO})_3$. *right:* Cristal structures of the starting comound and the products of an inverse electron demand Diels-Alder addition of $\text{TzPyRe}(\text{CO})_3\text{Cl}$ with Vinyl- and Ethynyl-ferrocene.

Another new approach for the CRC1333 is attaching molecules using a functionalized ligand that provides a direct ligand to surface connection. To this end we are currently developing a ligand that contains a tetrazine functionalists and with these, it is possible to synthesize metal complexes that can add an olefin or alkyne via an inverse electron demand Diels-Alder addition [3].

The Ringenberg group [4] published one of the first of these types of coordination compounds - including the first crystal structure of such addition products. The $\text{TzPyRe}(\text{CO})_3\text{Cl}$ was reacted with vinyl and ethynyl ferrocene and both the reactions take place at RT.

- [1] M. Ringenberg et al., *Inorg. Chem.*, **56**, 7501–7511 (2017)
- [2] Mario Winkler, submitted
- [3] P. Audebert et al., *Angew. Chem. Int. Ed.*, **57**, 12057-12061 (2018)
- [4] M. Schnierle, *ChemComm*, accepted. // DOI: 10.1039/d0cc03805a

The Electronic and Geometric Structure of Immobilised Catalysts

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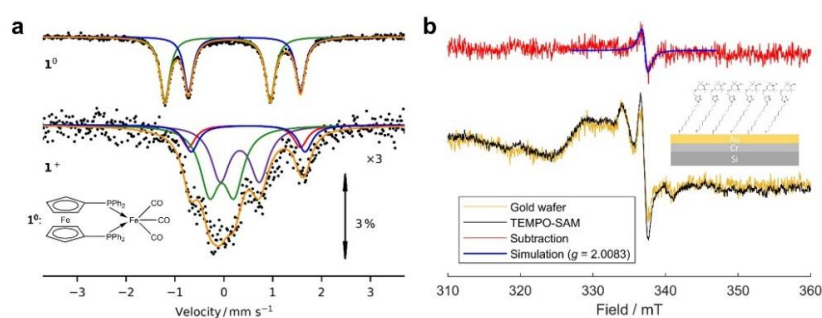


Figure 1: (a) Mössbauer experiment of the investigated catalyst in its neutral and oxidised form at room temperature showing the occurrence of two isomers of the latter. (b) EPR experiment of the immobilised TEMPO radical on a SAM showing only weak intensities due to a very low number of detectable radical species.

In order to understand the behavior of a chemically immobilised catalyst, one must be able to probe the chemical properties of the compound in its bound and free forms. This is why (dppf)Fe(CO)₃ was chosen as the catalytic system of interest. [1] We have studied the parent complex in neutral and +1 oxidation states by a wide range of spectroscopic techniques. [2] Temperature dependent Mössbauer measurements confirm the existence of two isomers at room temperature (Figure 1a) and slow relaxation of magnetisation at liquid helium temperature. Furthermore, it was shown via ENDOR spectroscopy that the counter ion [BAr^F₄], that is used frequently because of its non-coordinating character [3], does nevertheless show low distances to the unpaired electron on the carbonyl-iron in the range of 4.8(1) Å.

The incorporation of a simpler radical (4-Azido-TEMPO) into a COF, provided by project A3, [4] via click chemistry revealed an interaction of these radicals, leading to much different lineshapes due to exchange broadening or motional averaging from nearby spins and increased relaxation times of the magnetisation in pulsed EPR. This is likely a result of the small distances between the paramagnetic centers and a resulting dipolar coupling with the pore walls as this behavior can not be seen in the monomeric building block on which the immobilised radical was investigated as well.

Together with A2, TEMPO radicals were successfully immobilised on a self-assembled monolayer, again revealing strong intermolecular interactions between the radicals seen by the change of the line shape in the EPR experiment. Both experiments show the strong influence on the dynamics of the immobilised species.

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- [2] M. Winkler, submitted
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High Resolution Tomography of mesoscopic pore structures and self-assembled Monolayers

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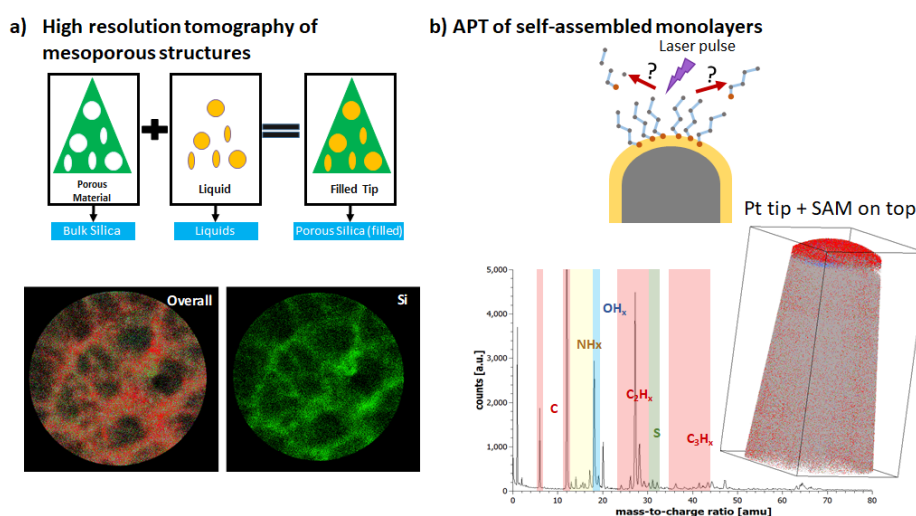


Figure 1: a) Schematic procedure preparation of porous APT samples and atom map of silica
b) Mass spectrum of a SAM and reconstructed atom map of SAM and Pt substrate.

a) High resolution tomography of mesoporous silica gel

In order to measure porous materials in atom probe tomography (APT), the pores need to be filled with a contrasting material. Therefore, based on a “water-absorbed sponge” principle, we present a potential method for the structural visualization of mesoporous materials by using liquid as the filling material. In this work, desiccant silica gel was selected due to its water adsorption. Lamella samples were firstly prepared from normal FIB-Liftout procedure and then wetted via moisture adsorption. Secondly the samples were instantly frozen to avoid the liquid drainage and then shaped into tips using cryo-FIB technique. The mass signals consisted mainly of the silanol group (Si-O-H)⁺ while the reconstructed atom map displayed an irregular porous-network structure. Moreover, the pore diameters were indeed in the required range, showing that APT measurement of porous materials is indeed possible.

b) Atom probe tomography of self-assembled monolayers

The second part focuses on the linkage of catalysts to the pores. To determine the binding, SAMs are investigated by APT. This project focuses on the physical understanding on the field evaporation of organic molecules under high electric fields, as they occur in APT. Next to the conventional thiol-metal system, SAM molecules of phosphonic acids, which bind to oxides, are investigated and compared for different measurement conditions. The carbon chains break under the influence of the high electric fields and small sized molecular fragments are detected. Measurements of cryo-prepared liquids of similar molecular structure show by contrast little fragmentation and the evaporation of the whole chain. This suggests different binding conditions, since the SAM molecules are anchored to the substrate, thus requiring higher evaporation fields and resulting in higher fragmentations.

Simulation of the Rhodium-catalyzed asymmetric 1,4-addition reaction mechanism

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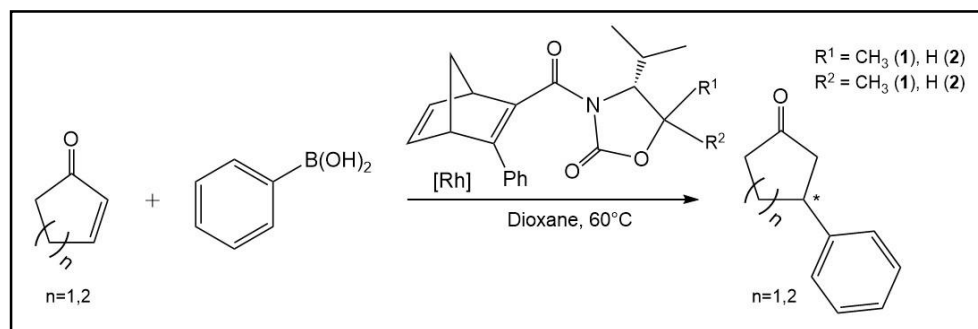


Figure 1: The 1,4-addition of phenylboronic acid to cyclic enones.

Theoretical studies on the Rh-catalyzed asymmetric 1,4-addition of phenylboronic acid to cyclic enones were performed using two newly synthesized catalysts **1** and **2** [1]. The ligands of the two catalysts both consist of a norbornadiene unit. Each ligand is asymmetrically substituted with a phenyl group and a different oxazolidinone derivative. Their difference is the presence of two methyl groups in one oxazolidinone unit. 2-cyclohexenone and 2-cyclopentenone were used as reactants.

A generally accepted cyclic four-step reaction mechanism includes at first a catalyst transmetalation (TM) step, where the phenyl group of the phenylboronic acid is transferred to the catalyst. It is followed by an enone-binding (EB) and a syn-carborhodation (CR) step, where the enone approaches the catalyst and bond formation takes place. Subsequently, enolate hydrolysis (EH) yields the arylated product and regenerates the catalyst.

Various possible reaction pathways were studied. The initial structures of these pathways were obtained from conformational searches of the EB step at GFN2-xTB level using the Conformer-Rotamer Ensemble Sampling Tool (CREST). These resulted in the distinction of the four binding modes η^2 -cis, η^2 -trans, ring and phenyl for the approach of the enone in the EB step. For each binding mode, the enone can approach the catalyst in a *re* or *si* orientation, which results in the (R)- or (S)-product, respectively. For 2-cyclohexenone, the C5-atom can either point upwards or downwards with respect to the ring plane, resulting in an additional degree of freedom. Thus, 16 pathways had to be studied for 2-cyclohexenone and 8 pathways had to be studied for 2-cyclopentenone. The CR step was studied in detail using the GFN2-xTB method for pre-optimizations and Density Functional Theory (DFT) calculations at the B3LYP/def2-SVP-D3(BJ) level for optimizations of minima and transition states. Energy calculations at the B2-PLYP/def2-TZVP-D3(BJ) level revealed that the η^2 -cis and η^2 -trans binding modes are favoured for both reactants and both ligands. The calculations of enantiomeric excesses (*ees*) were performed using the Gibbs energy barriers for the CR step with respect to the separated reactants and the catalysts after the TM step. These revealed an *ee* of 22% (R)-product for 2-cyclohexenone with catalyst **1**, while for 2-cyclopentenone *ees* of 98% and 88% for the (S)-product were obtained for catalyst **1** and **2** respectively. All *ees* are in good agreement with corresponding experimentally determined *ees*.

[1] M. Kirchhof, Katrin Gugeler et al., *Organometallics*, ASAP

Theoretical Study of Covalent Organic Frameworks and Field Evaporation of Organic Molecules

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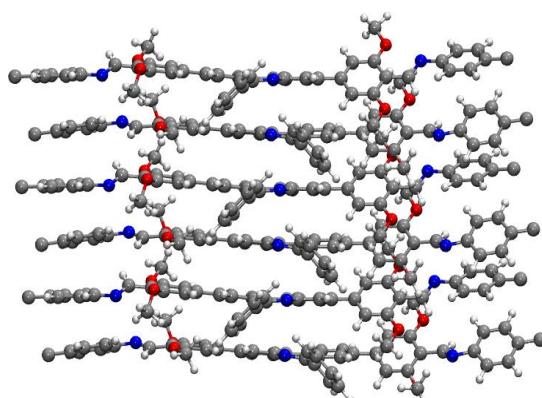


Figure 1: Example of the most stable arrangement of a unit cell side of a COF during the component analysis.

Covalent organic frameworks (COFs) are an emerging class of crystalline polymers which are used to construct porous structures. Within the framework of the CRC 1333 they are intended to act as a potential porous environment for catalytic reactions. In order to form porous structures, a stacking of several COF layers is necessary. In initial studies we observed that the interlayer interaction and the corresponding stacking behavior are predominantly determined by van-der-Waals interactions. Generally subsequent layers are shifted against each other to maximize favorable interaction sites. For COFs synthesized within project A3 structures as well as interlayer distances could be obtained. Furthermore, a component analysis for the Tpp-Tab COF was performed. Here, the possible arrangements of the COF's building blocks were analyzed by various methods to determine favorable orientations. It was found that arrangements with interacting linker groups forming a T-shape stacking and alternately arranged imine groups are energetically favorable, see Figure 1. Moreover, the addition of methoxy groups lowers the overall energy difference between parallel and anti-parallel imine arrangements and increases the overall interaction energy between layers.

Initial structure, cell parameters and partial charges were calculated for various COFs and are currently used to simulate the adsorption of gas molecules in COF systems by means of Monte Carlo simulations (cooperation with C5). Partial charges were also calculated after the COF was filled with gas molecules to investigate the polarizability of structures at hand.

In a different project the signal-generating process in atom-probe tomography was simulated. This is an emerging tool with the prospect of analyzing a surface at atomic resolution. The desorption and evaporation processes of self-assembled monolayers (SAMs) formed of thiolate molecules on a gold surface in strong electric fields were studied by means of DFT [1]. Desorption patterns for two different SAM-molecules were obtained. During the process, the charge was accumulated in the headgroups upon the breaking of covalent bonds and the evaporation of ions from the surface.

[1] Dietrich, Carolin; Schuldt, Robin; Born, Daniel; Solodenko, Helena; Schmitz, Guido; Kästner, Johannes "Evaporation and Fragmentation of Organic Molecules in Strong Electric Fields Simulated with DFT" submitted to J. Phys. Chem. A (2020)

Simulation of Atomic Probe Tomography

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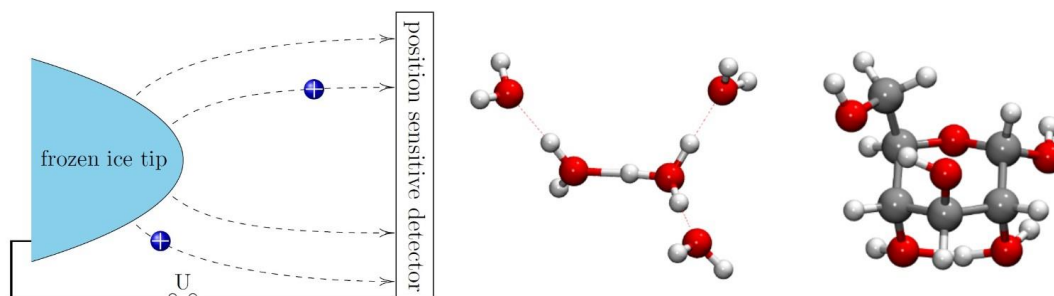


Figure 1: Setup of APT and charged water cluster and glucose molecule ($C_6H_{13}O_6^+$).

Atom probe tomography offers the opportunity to investigate solid materials with atomic resolution. Initially, this technique was used to investigate metals and has since evolved to measuring the composition of other materials such as semiconductors and self-assembled monolayers (SAMs) of organic molecules [1].

APT has the potential of being highly versatile in regard to the different kinds of materials it can measure, however, before complex organic materials, such as biomolecules or even entire cells can be investigated, the evaporation of pure water and solutions must be understood. By freezing the liquid, APT can be performed on water in similar fashion to other solid materials. Measurements reveal that even something as fundamental as pure water shows a complex evaporation behavior and thus calls for theoretical calculations to interpret the mass spectra. DFT calculations were performed to find stable molecule geometries corresponding to the measured mass-to-charge ratios. Additionally, conformational searches were conducted in order to find alternative molecule geometries.

In the case of pure water, the calculations found stable water clusters consisting of $H_3O^+ + n(H_2O)$, as well as a few metastable structures corresponding to the measured mass-to-charge ratios of 44 and 69 amu.

The investigation of glucose in solution showed a data peak at 181 amu corresponding to $C_6H_{13}O_6^+$ (which is glucose + H^+). Other structures correspond to said molecule with the addition or removal of one or more H_2O .

- [1] C. Dietrich, R. Schuldt, D. Born, H. Solodenko, G. Schmitz, J. Kästner, **Evaporation and Fragmentation of Organic Molecules in Strong Electric Fields simulated with DFT**, *submitted to J. Phys. Chem. A* (2020).
- [2] T. Schwarz, E. Weikum, K. Meng, E. Hadjixenophontos, C. Dietrich, J. Kästner, P. Stender, G. Schmitz, **Investigation of Frozen Pure Water Tips by Atom Probe Tomography**, *submitted to Sci. Rep.* (2020)

Computer simulation of adsorption in covalent organic frameworks

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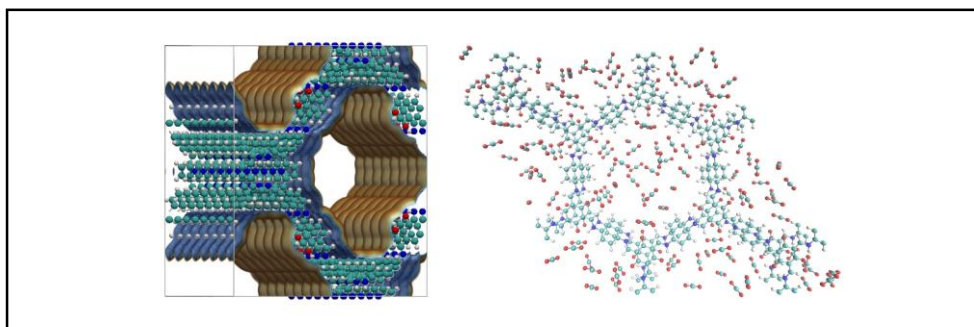


Figure 1: Illustration of a typical 1D channel structure of a covalent organic framework (left). Distribution of CO₂ molecules at high loading in COF TpPA (right).

Covalent organic frameworks (COFs) are crystalline porous materials serving as a promising platform for many applications, including catalysis. Using such frameworks as tunable scaffolds will be enhanced by a molecular picture of the effects of surface chemistry or catalyst loading on the distribution of reactant and product molecules. A molecular-level interpretation of the adsorption behavior of probe molecules such as Ar, N₂, CO₂, CH₄ or NO can be obtained from Monte Carlo simulations in the grand canonical ensemble. To obtain meaningful results several methodological obstacles have to be addressed that are solved in collaboration with subprojects A3 and C4. Moreover, an alternative approach to calculate adsorption isotherms, classical density functional theory [1], is assessed.

[1] E. Sauer, J. Gross, *Langmuir* **35**, 11690 (2019).

Molecular Simulation and Classical Density Functional Theory in Covalent Organic Frameworks

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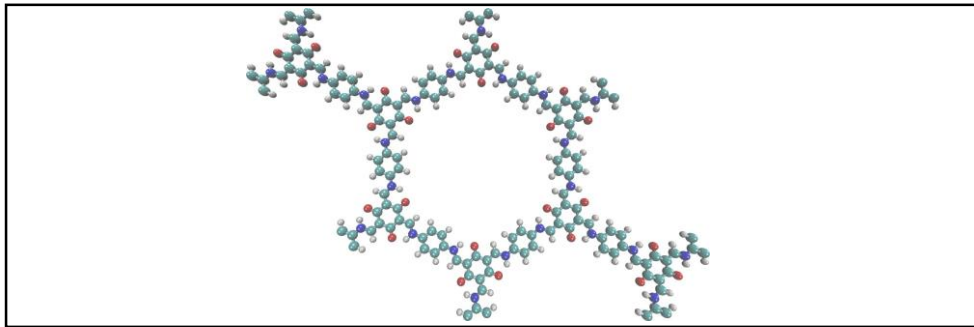


Figure 1: TpPa-1 COF

Molecular simulations on an atomistic level lead to a fundamental understanding of adsorption in porous media. As input a structure of the solid and a forcefield which models the fluid-fluid and the fluid-adsorbent interactions are needed. Due to the possibility of conducting unphysical moves Monte Carlo simulations (MC) are the tool of choice to study adsorption behavior. Using MC simulations static properties e.g. density profiles and adsorption isotherms can be predicted. In the last years great progress has been made simulating materials like zeolites, MOFs and lately also covalent organic frameworks (COFs).

Classical Density Functional Theory (DFT) is a fluid theoretical approach which allows to derive the previously mentioned properties. The density profile is obtained by minimizing the functional derivative of the grand potential with respect to the density profile. Excellent agreement between the two methods can be shown for model systems and for adsorption in COFs. DFT simulations are much less computational expensive and allow to conduct a larger amount of simulations to obtain e.g. pore size distributions. Especially the interplay between MC and DFT, where MC is used as a benchmark and DFT as a working horse can establish techniques for screening the numerous COFs for applications such as gas storage or separation.

Besides the mentioned realistic structures model systems are built and used to study the isolated impact of fluid or solid properties on adsorption behavior. One can investigate e.g. interlayer slipping effects in COFs or chemical heterogeneities of surfaces. Those studies allow to obtain a deeper molecular insight in adsorption phenomena.

Statistical Insights into Olefin-Metathesis Catalysis in Confined Geometries via Coarse-Grained Particle-Based Simulations

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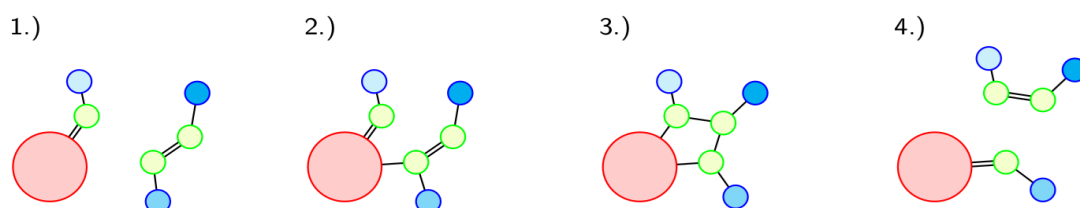


Figure 1: Reaction scheme of the model. The catalyst is illustrated in red, the particles which can exchange bonds are green and the different blue particles resemble the beginning of other molecules which will exchange ligands. 1.) A free particle chain approaches the catalyst. 2.) A bond is formed on collision of this particle chain and the catalyst. 3.) The ring with the earlier attached chain and the new chain is closed. 4.) The bonds break and the new chain is released.

We construct a particle-based method to model the olefine-methathesis catalytic reaction. The core feature is a reactive force field, which allows the creation of bonds on collision and the destruction of bonds at a defined rate. An example on how this method operates can be seen in figure 1. This model certainly lacks many chemical details, however it is very fast, which enables us to run long simulation to get better statistical insights into the outcome of these reactions.

With this model in hand we investigate the influence that geometric confinement has on balance between **Acylic-Dinene-Metathesis (ADMET)** and **Ring-Closing-Metathesis (RCM)**. These two reaction types occur when starting the reaction from an diene solution. ACMET will happen when the ends of two different molecules join together, while in the RCM case both ends of the same molecule bond together. The idea is that the geometric confinement changes the conformations the diene could be in and therefore shifts this equilibrium in favour of RCM. The experiments to these reactions are done Ziegler et al. [1] and we choose our parameters to recreate these results.

[1] F. Ziegler et al., J. Am. Chem. Soc. 2019, 141, 48, 19014-19022

Using Immobilized Ru Hydride Complexes to Understand the Interaction of Molecular Heterogeneous Catalysts with Pore Walls under Catalytic Conditions

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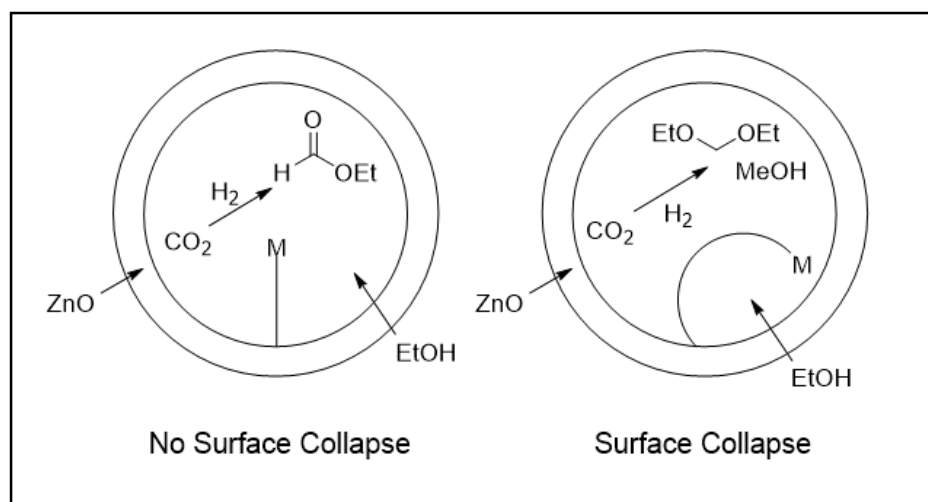


Figure 1: Effect of surface collapse on catalytic active species immobilized onto functionalized mesoporous materials.

Homogeneous catalysts immobilized in porous support materials often have much lower activity on the surface versus in solution. In many cases, this is likely due to surface collapse, or the undesired interaction between catalyst and support material. However, measuring surface collapse experimentally is challenging, making it difficult to understand the experimental conditions under which surface collapse occurs. In order to address this, we have developed catalytically-active Ru complexes that can be linked to the surface of porous supports that have a strong metal-support interaction with Lewis acidic sites on the support surfaces. These ruthenium polyhydride catalysts are tethered inside pores of mesoporous materials and subsequently analyzed using IR, MAS NMR, and XAS. Using the change in activity/selectivity of the catalyst upon surface collapse as an in-situ probe, we can directly measure the effect of various experimental factors on surface collapse, such as linker length, linker rigidity, solvent, and reaction temperature.

Hard X-ray spectroscopy of molecular heterogeneous catalysts in mesoporous materials

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The goal of the CRC1333 is to perform heterogeneous catalysis in mesoporous materials by immobilizing molecular catalysts inside the pores and using confinement effects as key factor for selectivity. Both pore size and pore geometry are expected to have a significant impact on the reactivity as well as the coordination chemistry of the immobilized catalysts. In project S1, spectroscopy with hard X-rays is used to analyze these influences based on the excitation of electrons close to the atom nucleus, mainly the 1s-electrons. Hard X-rays enable the investigation of the molecular nature of catalytic complexes fully independent of the state of aggregation. The spectroscopic methods used in project S1 include XANES (X-ray absorption near structure) to get information about the oxidation state of the central atom and EXAFS (Extended X-ray absorption fine structure) to illustrate bond distances as well as type and number of the coordinating atoms. Moreover, HERFD-XANES (high energy resolution fluorescence- detected XANES) and vtc-XES (valence-to-core X-ray emission spectroscopy) provide the HOMO- and LUMO energies of the complexes and ctc-XES (core-to-core X-ray emission spectroscopy) enables the identification of their spin states (figure 1). The obtained data allow the comparison of the electronic and structural parameters of the molecular complexes in solution and inside the pores to get a deeper insight in the reaction mechanisms of the investigated catalytic reactions.^[1]

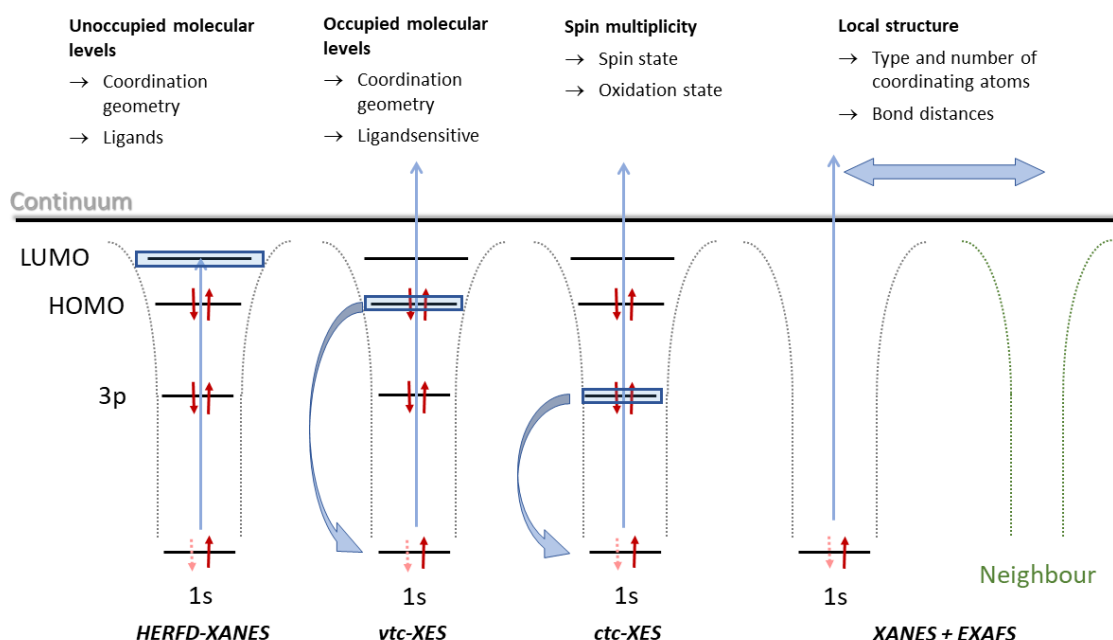


Figure 1: Hard X-ray methods and provided information for the example of K-edge spectroscopy.^[1]

[1] M. R. Buchmeiser, B. Plietker, CRC1333 Proposal *Molecular Heterogeneous Catalysis in Confined Geometries* 2018, 361-374.

The influence of ionic liquids on confined catalysts on the surface of the nano-size pore through atomistic simulations

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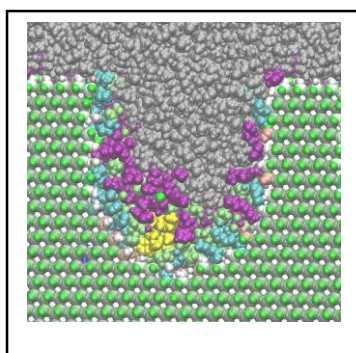


Figure 1: Snapshot of the simulation. Catalyst: yellow, [BMIm]⁺: Purple, [Otf]⁻: Cyan

We investigate the immobilization of catalysts in confined media in an ionic liquid (IL)-mixture following similar experimental investigations with other types of solvents [1]. Specifically, we study the mixture of n-heptane and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIm]⁺[Otf]⁻) in a closed pore geometry with a pore diameter of 5nm. The inner walls of the pore are functionalized in order to tune the polarity of the pore and its corresponding interaction with the solvent. The immobilization of the catalyst is expected to lead to higher turnover rates in the respective catalysis. Using atomistic Molecular Dynamics simulations, we model the catalyst in the IL-heptane mixture within the nanopore.

Our simulations reveal that the IL accumulates in the pore in combination with the surface functional groups. Accordingly, the catalyst is expected to be captured by this IL layer on the surface and be immobilized into the pore. Using quantum mechanical calculations, we parameterize a force-field for a Ru-based catalyst [2], which is being further used for a more accurately modeling of the catalyst within the IL-mixture in the pore.

Our results provide important information on the influence of steric and IL-specific effects, the structuring of a varying solvent environment, the pore functionality/polarity, and their synergistic interactions with the catalytic center. These aspects promote a deeper understanding on the micro-details towards a rational design of the catalyst immobilization and the relevant conditions. We discuss the possibility of a linker-free immobilization of catalysts in nanometer-sized regions through the supported ionic liquid phase technology.

[1] F. Ziegler et al., J. Am. Chem. Soc. 2019, 141, 48, 19014-19022
[2] Buchmeiser et al., Macromol. Chem. Phys. 2013

An atomistic view on liquid phase adsorption

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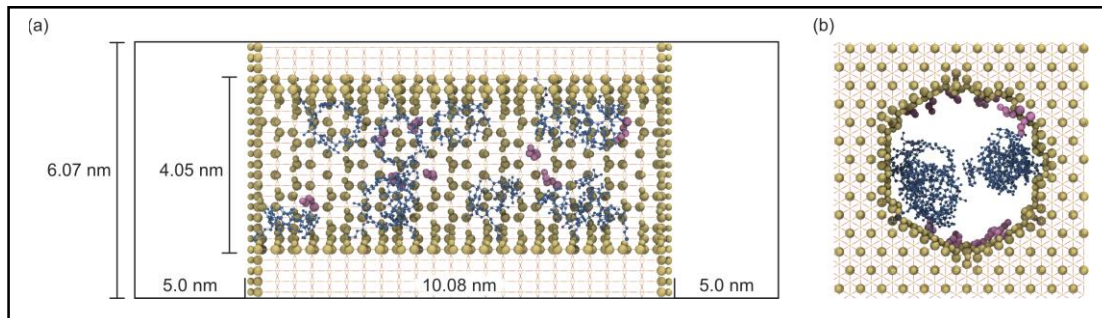


Figure 1: Pore system functionalized with five β -cyclodextrin groups using the surface linker proposed by Trofymchuk et al. [2] filled with water and benzene molecules, viewed from (a) the side and (b) the front.

The purpose of this project is to investigate the feasibility of calculating adsorption isotherms from the liquid phase using atomistic simulations. Here we study adsorption of aromatic molecules in a mesoporous silica support with and without β -cyclodextrin functionalization.

Huq et al. [1] reported that *p*-nitrophenol inside a non-functionalized silica pore does not adsorb onto the surface, whereas in a cyclodextrin functionalized pore, *p*-nitrophenol adsorbs onto cyclodextrin. On the other hand, Trofymchuk et al. [2] reported the presence of immobilized β -cyclodextrin groups on the inner pore surface increases the benzene adsorption ability of synthesized materials, thus concluding that cyclodextrin functional groups have a higher adsorption capacity compared to the bare surface.

These effects were observed in molecular dynamics simulations of pore systems (seen in Figure 1) generated by the python package PoreMS [3]

- [1] R. Huq, L. Mercier, and P. J. Kooyman. *Chem. Mater.* **13**, 12 (2001).
- [2] I. Trofymchuk, N. Roik, and L. Belyakova. *Nanoscale Res. Lett.* **12**, 1 (2017).
- [3] H. Kraus and N. Hansen. Porems: 0.2.0 (2020). doi: 10.5281/zenodo.3984865.