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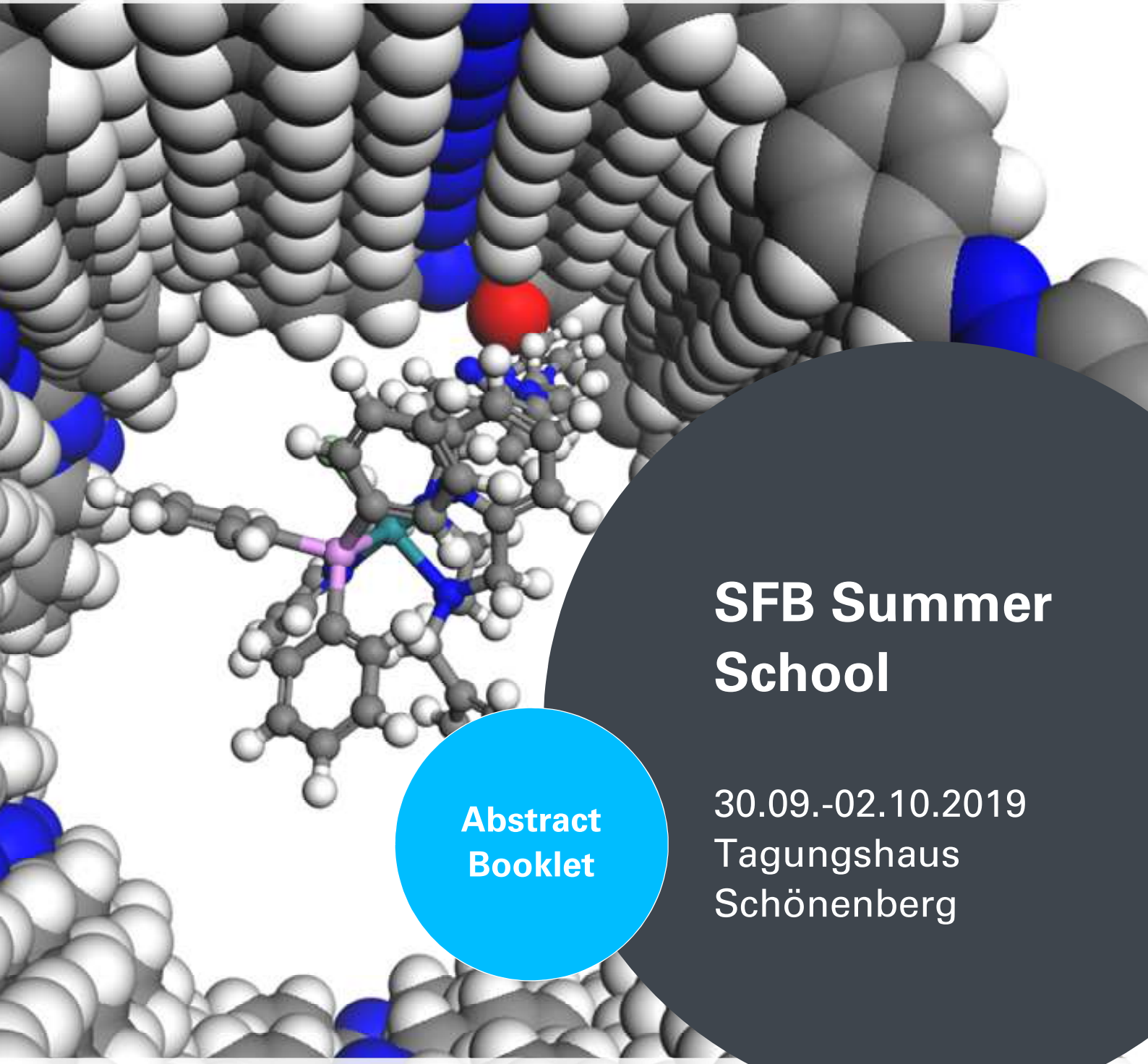

SFB Summer School

Abstract Booklet

30.09.-02.10.2019
Tagungshaus
Schönenberg

CRC 1333
Molecular Heterogeneous Catalysis in Confined Geometries
University of Stuttgart

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Introduction to catalyst design

Vera Meynen

Laboratory of Adsorption and Catalysis, Departement of Chemistry, University of Antwerp, Belgium

To introduce catalyst design, we will first discuss the importance of setting the criteria of the catalytic process. To assure good functioning of industrial catalytic processes, the whole of the process including various aspects of the catalyst, the reactor and the process needs to be taken into account. Once these criteria are set, the type of catalyst can be selected going more and more into detail on the design of the catalytic material itself, while always keeping the entire process in mind.

After introducing the catalytic process concept, we will focus on heterogeneous catalysts. The steps that are involved in the development of heterogeneous catalysts will be briefly introduced and the most important requirements for the formation of the catalyst will be discussed. Here, we will elaborate on the role of the active element, the carrier material (support) and promoters. Some examples of synthesis methodologies will be touched upon. Last, but not least, shaping of catalysts will be discussed.

At the end of this part, you should be able to roughly select important key aspects to design a catalyst from the macro to the nano scale (e.g. metal support interactions and catalyst dispersion) for a certain process and indicate where structural and physicochemical properties can impact performance. We will touch upon examples of innovative catalyst design to tackle challenges in recent trends to replace precious metals (e.g. in automotive catalysis), to inspire you how new designs can solve these issues. Finally, the concepts of catalyst design will be challenged in emerging technologies such as plasma catalysis, requiring additional material property-performance correlations, going beyond the concepts of thermal catalysis.

Elucidating Catalysis with Theoretical Chemistry and Computational Spectroscopy

Vera Krewald

Fachbereich Chemie, Theoretische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 4, 64287 Darmstadt

Computational chemistry has reached predictive power over the past decades and is seen by many as an important aid for the interpretation of experimental data. Of particular interest for catalytic processes is to elucidate the identity of transient intermediates and thus the reaction mechanism through a combination of spectroscopies and computations. In this talk, an overview of the capabilities and limitations of computational methods ranging from density functional theory to wavefunction approaches will be given.

Through a series of showcases focused on molecular transition metal chemistry, it will be illustrated how computational chemistry can describe the geometric and electronic structures of such complexes even in complicated scenarios. It will be discussed how to choose a suitable computational approach, taking into consideration desired accuracy and required computational effort. In the context of density functional theory, methods for the consideration of solvation, relativistic and dispersion effects are introduced. Going beyond single-determinant approaches, key concepts of complete active space methods are introduced.

The showcases include UV-vis spectroscopy of transition metal complexes for nitrogen fixation, X-ray spectroscopy of enzymatic active sites, Mößbauer spectroscopy for oxygen reduction at graphene-embedded iron sites, and magnetic coupling in manganese clusters.

A1: Monolithic polymeric supports with uniform pore diameter and tailored functional groups

Hande Açıkalın[1], Michael R. Buchmeiser[1]

[1]*Institut für Polymerchemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart (Germany)*

Monolithic polymeric materials have gained a strong position in materials science, in particular in the areas of separation science and heterogeneous catalysis. [1-2] When used in heterogeneous catalysis, catalysts must be located at the surface of the structure-forming microglobules in order to be accessible for reactants.

In view of the dimensions of typical organometallic catalysts (ca. 1.5 nm), the use of mesoporous materials is evident. [3-4] Ideally, a concept based on mesoporous materials retains the full flexibility of the catalyst but at the same time provides sufficient levels of confinement to generate the desired conditions.

With regards to that, the main goal is the realization of polymeric monolithic materials with defined, unimodal porosity in the range of 5-20 nm with transport pores in the micrometer range. Suitable anchoring groups for the immobilization of the catalysts must be selectively allocated in a spatially defined way inside the pores.

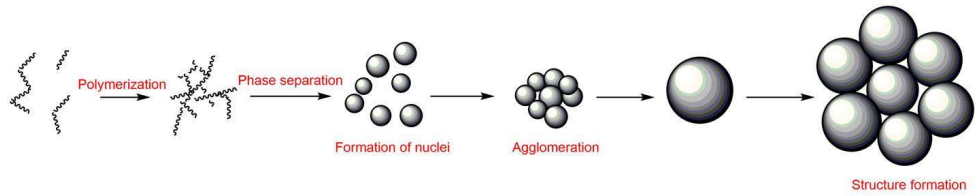

Figure 1: Formation of a polymeric monolithic structure and tailoring of the porosity.

[1] E. B. Anderson et al., *ChemCatChem* **2012**, *4*, 30-44
[2] T. B. Tennikova et al., *J. Liq. Chrom. & Rel. Technol.* **1990**, *13*, 63-70
[3] G. Y. Yang et al., *J. Am. Chem. Soc.* **2010**, *132*, 8129-8136
[4] J. Yuan et al., *Organometallics* **2016**, *35*, 2149–2155

A2: Block Copolymer Templating for Electrochemical Applications

Sherri Liu[1], Klaus Dirnberger[1], Sabine Ludwigs[1]

[1]*IPOC-Functional Polymers, Institute of Polymer Chemistry, University of Stuttgart, Germany*

Project **A2** aims to prepare nanoporous templates with tunable aspect ratios from etchable block copolymer systems of poly(styrene)-*block*-poly(lactide) (PS-*b*-PLA) and poly(styrene)-*block*-poly(methylmethacrylate) (PS-*b*-PMMA) for molecular heterogeneous catalysis in confined geometries (Figure 1). We proceed with optimizing the thin film production of highly ordered nanoporous templates of cylinder forming PS-*b*-PMMA supported by Au-coated silicon wafers as a fundamental system while PS-*b*-PLA to be synthesized by Lukas Stein is the final block copolymer system. The alignment of these PS-*b*-PMMA films uses an electric field while annealing above the glass transition temperature (T_g). [1,2] The conformation of cylinders that are perpendicular to the substrate are affirmed by hexagonally ordered pore structures.[3] After UV degradation of the minority PMMA domains, the surface morphology of etched PS-*b*-PMMA films will be analysed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). A self-assembled monolayer (SAM) of alkyl-azidothiols will be immobilized on the Au substrate followed by "Click"-chemistry with alkyne ferrocene to study the diffusion of redox-active units in confined geometries. [4] The presence of an azide absorption at 2100 cm^{-1} under infrared reflectance absorbance spectroscopy (IRRAS) indicates the success of clicking. [5] The electrochemical behavior of ferrocene-functionalized Au surface is investigated using scan-rate dependent cyclic voltammetry (CV) and the efficiency of aligned block copolymer templates for application as nanoporous templates will be examined. [6]

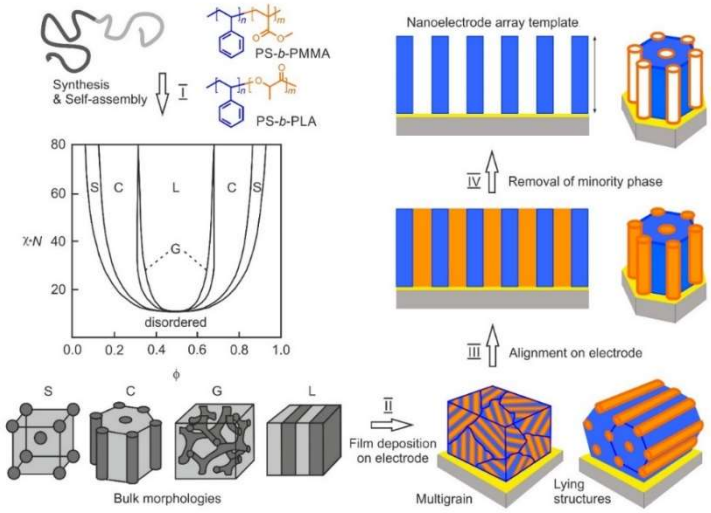

Figure 1: Schematic of the thin film production route of a nanoporous array template which will be further utilized as template diffusion studies with redox-active probe by scan-rate dependent cyclic voltammetry.

[1] T. Thurn-Albrecht et al., *Macromolecules* **2000**, *33*, 3250–3253
[2] T. Thurn-Albrecht et al., *Science (80-.).* **2000**, *290*, 2126–2129
[3] T. Thurn-Albrecht et al., *Adv. Mater.* **2000**, *12*, 787–791
[4] J. P. Collman et al., *Langmuir* **2004**, *20*, 1051–1053
[5] L. Bertilsson et al., *Langmuir* **1993**, *9*, 141–149
[6] H. C. Maire et al., *Polymer (Guildf).* **2009**, *50*, 2273–2280

A2: Synthesis and Self-Assembly of PS-*b*-PLA Block Copolymers

Lukas Stein[1], Rong Wu[1], Philip Dreier[2], Sherri Liu[1], Klaus Dirnberger[1], Holger Frey[2], Sabine Ludwigs[1]

[1]*Institute of Polymer Chemistry (IPOC), Pfaffenwaldring 55, 70569 Stuttgart, Germany*
[2]*Institute of Organic Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz, Germany*

Living anionic polymerization can be used to obtain well-defined block copolymers with tunable block chemistry, block ratios and molecular weights. The combination of block copolymer (BCP) structure formation by self-assembly and degradation of the minority block allows to create mesoporous BCP templates that are highly ordered with tunable pores which are promising to study molecular heterogeneous catalysis in confinement and electrochemistry in pores.

Polystyrene-*block*-polylactide (PS-*b*-PLA) systems are employed due to their large Flory-Huggins interaction parameters and soft etching capabilities of the PLA block. The synthesis involves the living anionic polymerization of hydroxyl functionalized PS followed by the ring-opening polymerization (ROP) of D,L-lactide.

For self-assembly the method of solvent vapor annealing is used to produce well defined morphologies on thin film BCP templates. [1] The surface morphology is then analyzed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) to verify a vertical cylindrical structure indicated as a hexagonal pore order.

Since a major goal of the CRC 1333 is to reduce pore diameters in order to achieve the desired confinement, miktoarm architectures are targeted. The polymer architecture can influence the size of the ordered domain features, which could enable access to PS-*b*-PLA templates with domain features smaller than 20 nm.[2,3] Therefore, we synthesized in a cooperation with the Frey group in Mainz, PS with varying hydroxyl end-functionalization, to access PS-*b*-PLA miktoarm BCP. Later the differences of the polymer architecture on the microphase separation behavior in bulk and in thin film templates should be investigated.

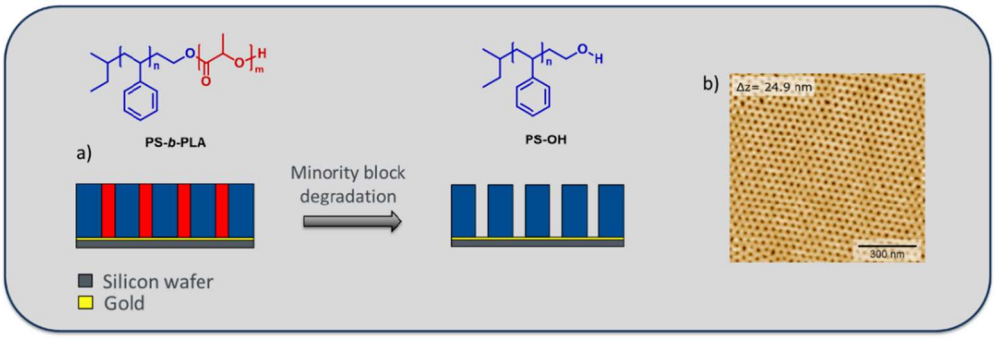

Figure 1: Schematic images of minority block degradation (a) and AFM height picture of a PS-*b*-PLA template obtained by solvent vapor annealing (b).

[1] A. Baruth et al., *ACS Appl. Mater. Interfaces* **2014**, *6*, 13770.
[2] M. W. Matsen, *Macromolecules* **2012**, *45*, 2161.
[3] W. Shi et al., *ACS Macro Lett.* **2015**, *4*, 1287.

A3: A Systematic Real-time *In Situ* Investigation of Mechanochemical Formation of Covalent Organic Frameworks

Sebastian T. Emmerling[1,2], Luzia S. Germann[1], Martin Etter[3], Robert E. Dinnebier[1], Bettina V. Lotsch[1,2]

[1]*Nanochemistry Department, Max Planck Institute for Solid State Research, 70569 Stuttgart,* [2]*Department of Chemistry, Ludwig-Maximilians-Universität München, 81377 München,* [3]*German Electron Synchrotron, Helmholtz Association of German Research Centres, 22607 Hamburg*

Covalent organic frameworks (COFs) are an emerging class of porous, crystalline 2D and 3D framework materials, consisting only of organic building blocks connected by strong covalent bonds. [1] The linkages between building blocks are made by reversible condensation reactions. COFs are usually synthesized solvothermally, requiring long reaction times, harsh conditions, and a large amount of solvent. As green alternative to conventional solution-based chemical synthesis, mechanochemistry undergoes a period of rediscovery. [2] Recently, mechanochemistry in form of liquid-assisted grinding (LAG) was used for the first COF syntheses. [3] With reduced reaction times and solvent amounts, the mechanochemical synthesis of COFs provides a practical and environmentally friendly alternative compared to the solvothermal approach.

Here, we provide the first systematic *in situ* study of the mechanism of mechanochemical synthesis of 2D and 3D COF formation involving systematically chosen building blocks forming 2D and 3D frameworks. Using *in situ* PXRD at the P02.1 beamline (DESY, Hamburg), we are able to provide detailed insights into the formation of COFs and reaction intermediates during the mechanochemical formation using LAG additives. The real-time investigation gives insights into the reaction kinetics and mechanism of the mechanochemical synthesis of COFs.

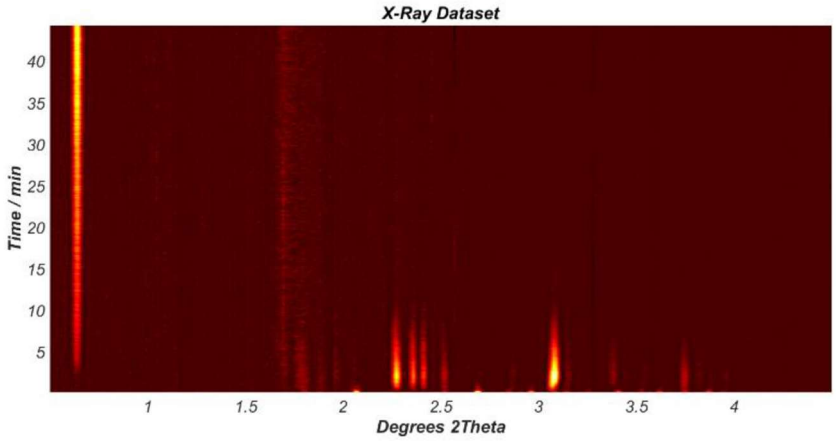

Figure 1: *In situ* monitoring of the formation of a covalent organic framework, measured in a ball-milling setup at the P02.1 beamline at DESY, Hamburg. The formation of the 2D COF can be followed by tracking its most intense (100) reflection and a molecular, crystalline reaction intermediate can be observed.

[1] A. P. Côté et al., *Science* **2005**, *310*, 1166-1170.
[2] J.-L. Do et al., *ACS Cent. Sci.* **2017**, *3*, 13-19.
[3] G. Das et al., *Chem. Commun.* **2014**, *50*, 12615- 12618.

A3: Versatile Synthesis of Isoreticular Covalent Organic Frameworks with Various Mixable Functional Moieties

Alexander M. Pütz[1,2], Frederik Haase[3], Tanmay Banerjee[1], Bettina V. Lotsch[1,2]

[1]*Nanochemistry Department, Max Planck Institute for Solid State Research, 70569 Stuttgart,*
[2]*Department of Chemistry, Ludwig-Maximilians-Universität München, 81377 München,*
[3]*Institute for Integrated Cell-Material Sciences, Kyoto University, 606-8501 Kyoto, Japan*

Like other porous materials, covalent organic frameworks (COFs) are effective materials for gas storage and heterogeneous catalysis, [1,2] among others. Their high porosity, surface area, structural customizability, and high recyclability particularly recommend COFs for catalysis. The incorporation of organocatalytic or metal-organic catalytic groups into COFs is typically achieved by postfunctionalization, i.e., by modification of pre-installed functional groups. [3] For imine COFs, a deliberate choice of linkers can yield defect structures, which introduce residual amine or carbonyl moieties into the lattice. [4,5] Functional groups that show orthogonality towards the reticulating reaction can, however, be introduced more straightforwardly. [6]

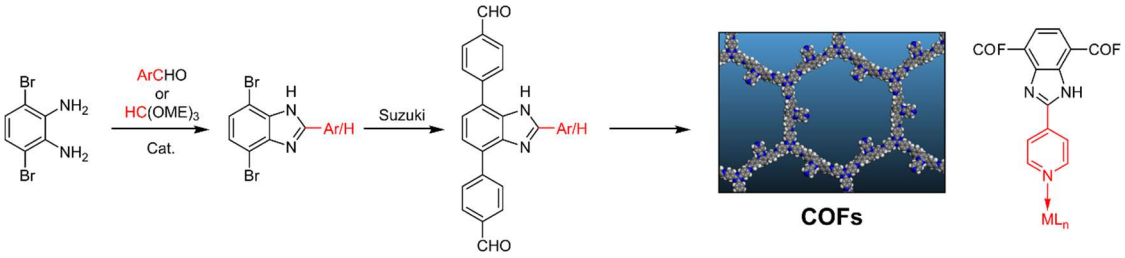

Figure 1: A single divergent synthetic pathway is used to access various benzimidazole-based covalent organic frameworks. They can be further augmented via the coordination of metal centers to pore-wall integrated functional moieties.

We developed a divergent synthesis pathway for functionalized benzimidazole building blocks based on 3,6-dibromobenzene-1,2-diamine as a versatile starting material. This work comprises the synthesis and characterization of imine-linked COFs based thereon. They feature various pore wall-incorporated (hetero-) aromatic functionalities that can serve to coordinate metal centers or attach other moieties. We expect additional applications of this synthetic method for other functional groups and catalytic moieties.

[1] L. Stegbauer et al., *Chem. Mater.* **2015**, *27*, 7874.
[2] V. S. Vyas et al., *Nat. Commun.* **2015**, *6*, 8508.
[3] H. Xu et al., *Nat. Chem.* **2015**, *7*, 905.
[4] T. Banerjee et al., *Nat. Commun.* **2019**, *10*, 2689.
[5] B. Zhang et al., *J. Am. Chem. Soc.* **2019**, *141*, 11420.
[6] C. S. Diercks et al., *Science* **2017**, *355*, eaal1585.

A4: Optimized Synthesis and Functionalization of Mesoporous Silica Materials

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In the past, ordered mesoporous silica materials (MSMs) have received substantial scientific interest due to their superior thermal and chemical stability. This is the reason why they are used in the CRC 1333. The bio-inspired concept of the CRC 1333 is the anchoring of organometallic catalysts within the pores of different mesoporous materials.[1] The standard synthesis route to mesoporous silica materials is the "cooperative self-assembly" route using block copolymers as template.[2]

For the attachment of the organometallic catalysts on the pore walls, the functionalization of the external and especially of the internal surface is necessary. There are many different processes thinkable to modify the surface of MSMs. A possible way is to inertize the silanol groups at the external surface for example with trimethyl-chlorosilane before the organic surfactant would be removed from the pores. In a second step, the internal surface would be functionalized by direct exchange of the template with the silane *via* template displacement with orgganosilanes (TDS).[3] The used catalyst should contain a functional group which is useable for the click-reaction with the organometallic catalysts. Another possible route to functionalize the carrier material is the removal of the shaping template *via* calcination or extraction before functionalization of the internal surface with the matching silane. Therefore, the immobilization of the external surface is neccessary. The different methods to modify the mesoporous silica material will be evaluated in order to ensure a controlled surface functionalization regarding the concentration and distribution of catalyst on the surface.

[1] https://www.crc1333.de.
[2] V. Meynen et al., *Microporous Mesoporous Mater.* **2009,** *125*, 170.
[3] V. Antochshuk et al., *Chem. Mater.* **2000**, *12*, 2496-2501.

A4: Controlled synthesis of mesoporous silica materials by liquid crystal templating

Johanna R. Bruckner[1], Jessica Bauhof[1], Ann-Katrin Beurer[2], Yvonne Traa[2], Frank Giesselmann[1]

[1]*Institute of Physical Chemistry, University of Stuttgart, 70550 Stuttgart, Germany*
[2]*Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany*

Hexagonal lyotropic liquid crystals (LLCs) are formed by a regular array of rod shaped micelles with their long axes being aligned along a common direction. Thus, they are ideal templates for the synthesis of mesoporous materials. An added silica precursor which solely dissolves in the continuous aqueous phase, polycondensates around the micelles during hydrothermal treatment. After removing the template, an inverse of the former hexagonal LLC phase is obtained. Such mesoporous silica materials can be used for a variety of applications, e.g. energy storage, synthesis of nano-particles, adsorption or drug delivery. Furthermore, they play a key role in the CRC 1333 [1] as carrier materials for catalysts. Concerning these materials, a precise control of the pore size and shape is crucial for the success of the project.

Even though there are some publications about lyotropic liquid crystal templating [2], only little is known about the templating process itself as well as the correlation between the LLCs and the mesoporous material's structure. Therefore, we systematically investigate various synthesis methods and production parameters while analyzing intermediate and final products as well as the corresponding LLC phases by a wide range of methods such as SAXS, N_2-adsorption and TEM (see Figure 1). Our study provides new insights into the role of the LLC phases in the templating process and improve the tailored design of new mesoporous materials.

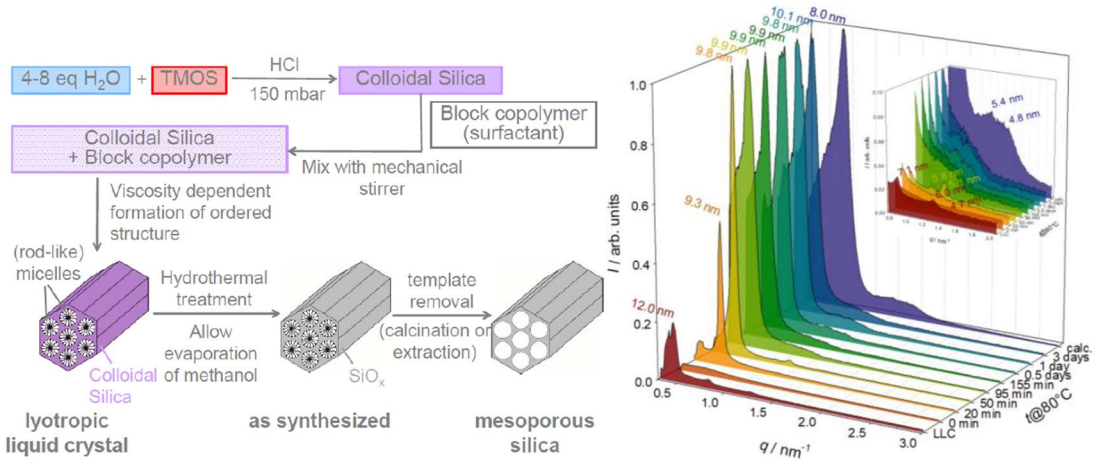

Figure 1: A new process had to be established for templating with highly viscous lyotropic liquid crystals (left). Time resolved SAXS measurements of the former give insight into the structural changes during the templating process (right).

[1] https://www.crc1333.de/
[2] G. S. Attard et al., *Nature* **1995**, *378*, 366-368;
P. Feng et al., *Langmuir* **2000**, *16*, 5304-5310;
S. G. Wainwright et al., *Microporous and Mesoporous Materials* **2013**, *172*, 112-117.
[3] Financial support by the DFG (CRC1333) is gratefully acknowledged.

A5: Organic-inorganic hybrid materials with tunable pore size as catalyst supports

Petia Atanasova[1], Yaseen Qawasmi[2], Karina Abitaev[2], Thomas Sottmann[2], Joachim Bill[1]

[1]Institute for Materials Science, University of Stuttgart, Stuttgart, Germany, [2]Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany

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 will be 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, TiO_2, SiO_2, ZrO_2 and Al_2O_3 to adjust the pore size. Alternatively, inorganic mesoporous supports as inverse replica of polymer foams and colloidal crystals (project **A7**) with different pore geometry 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**)) will be studied.

Here, we present the working plan of the project accompanied by our first experimental results. The synthesis of mono- and bimodal inverse opals (Figure 1), SAM formation on thin oxide films and mineralization of mesoporous polymer foams is discussed, and the main issues faced during this work are addressed.

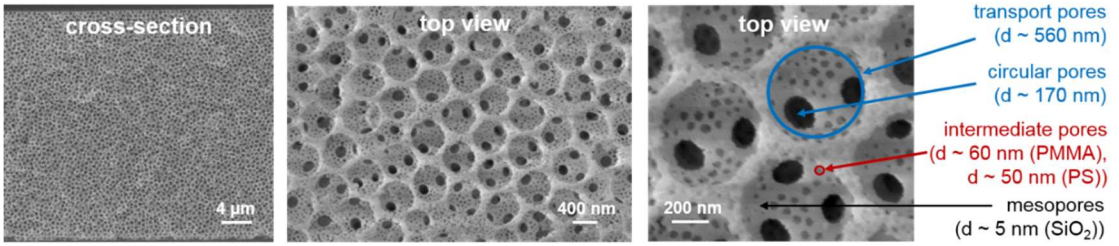

Figure 1: Cross-section and top view SEM images of bimodal silica inverse opal with a hierarchical structure including big transport and circular pores, intermediate pores and mesopores.

[1] Y. Qawasmi et al., *Sci.* **2018**, *296,* 1805

A6: Porous Carbons by Block Copolymer Templating

Felix Markus[1]

Institute of Polymer Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Organic soft-templating approach as described by Dai and Zhao.[1-2] Pluronic-type polyethers are employed as structure-directing agents (SDAs). The mesostructure is fixed by cross-linking of phenolic resins (= carbon precursor). At T = 700 °C the material is carbonized, whereby the less dense, oxygen-rich PPO-formed channels are burned off. This strategy works for both regular Pluronics ($PEO_{m/2}$-PPO_n-$PEO_{m/2}$) and Reverse Pluronics ($PPO_{n/2}$-PEO_m-$PPO_{n/2}$).

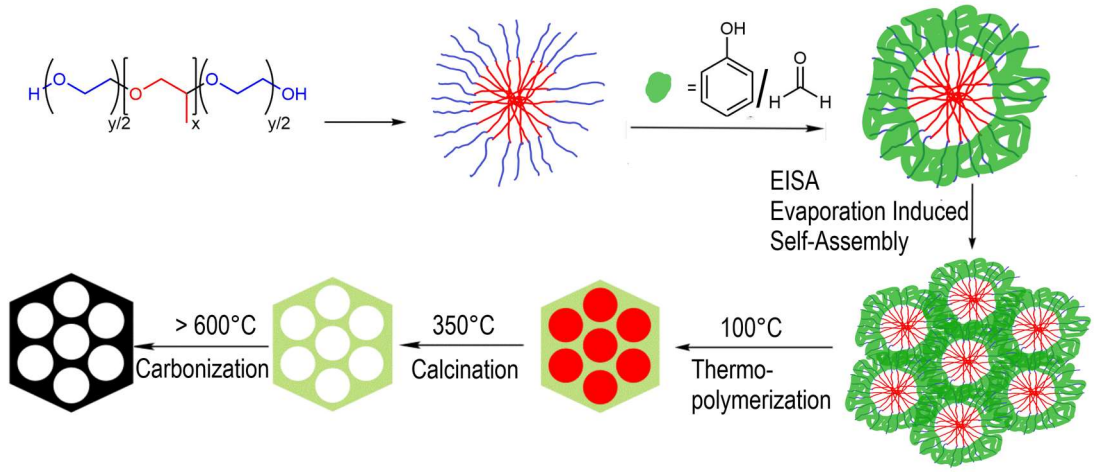

Figure 1: Here goes the caption

A7: Nanoporous host materials with adjustable pore size, geometry and distribution: synthesis, functionalization and characterization

Karina Abitaev[1], Thomas Sottmann[1]

[1]*Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart (Germany)*

Within the CRC 1333, our group is aiming to provide tailor-made mesoporous polymer and organic/inorganic hybrid supports. Therefore, we utilize colloidal crystals of polymer nanoparticles which are transferred into a porous polymer, following the NF CID principle [1]. The influence of the particle size (d_{part}), polydispersity (PDI) and ordering of the colloidal crystal on the obtained porous polymers was investigated. Polystyrene nanoparticles were synthesized by emulsion polymerization at various conditions. The dispersion was then gently dried at isothermal conditions, leading to the formation of closely packed colloidal crystals. The nanoparticle properties, e.g. d_{part} and PDI were found to be strongly dependent on the surfactant concentration and type. Investigations on the corresponding colloidal crystal structure showed that higher PDI results in the loss of the packing order whereas the packing density increases. Interestingly, foaming experiments revealed that colloidal crystals of small particles with a moderate PDI generate the porous polymer with smaller pores. However, the smallest pore size produced following this method so far is about 80 nm. Thus, the applicability of alternative approaches will be studied. On the one hand, self-assembled nanostructures of microemulsions, e.g. the bicontinuous or L_α structure with length scales of 1 nm to 100 nm will be utilized as 1-to-1 template for porous polymers [2,3]. One the other hand, monodisperse polymer nanoparticles and their colloidal crystals will be utilized for the synthesis of inverse opals or mesoporous materials in cooperation with **A5**.

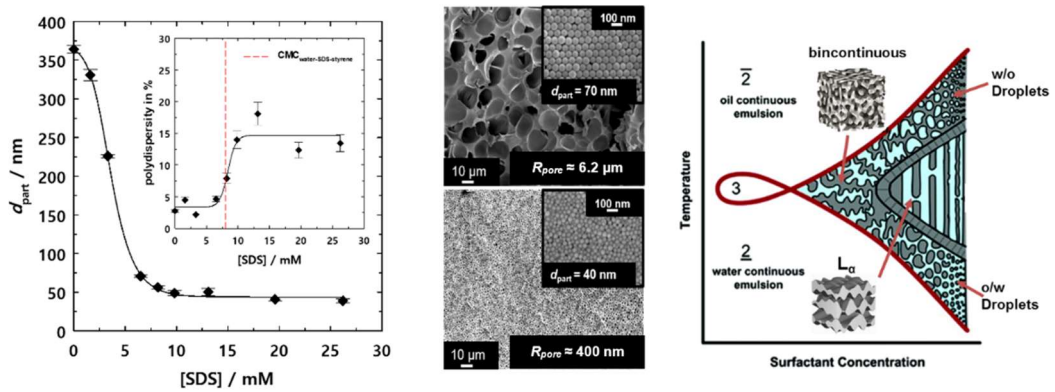

Figure 1: Polystyrene particles with 40 ≤ d_{part}/nm ≤ 450 and 3% ≤ $PDI_{d,part}$ ≤ 25% were synthesized (left) and foamed via NF-CID at T = 55 °C, p = 250 bar and t_{sat} = 15 min. For colloidal crystals of monodisperse particles large pores were obtained, whereas a homogeneous porous structure was obtained utilizing small and polydisperse particles (middle). In an alternative approach, nanostructures of microemulsions will be used as template to generate porous supports (right).

[1] R. Strey et al., *DE Pat*. **2010**, 102 010 053 064 A1
[2] F. Gao et al., *Journal of the American Chemical Society* **2004**, *126*, 12746.
[3] R. Schwering et al., *SÖFW-Journal* **2009**, *135*, 43-53.

A7: Confined Geometries of Nanofoams and Microemulsions for Molecular Heterogenous Catalysis

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The aim of our project within the CRC 1333 is to take advantage of the confined structures in polymeric nanofoams and reaction-specific microemulsions to study and understand the confinement effect on molecular heterogenous catalysis.

The first part of this study focuses on the synthesize of polystyrene nanofoams following the *Nanofoams by Continuity of Inversion of Dispersion* (NF-CID) method [1]. The fundamental idea behind NF-CID is the use of close-packed colloidal crystals of thermoplastic polymer nanoparticles as a template, exclusively utilizing the voids between the nanoparticles for the accumulation of CO_2 molecules. Ideally, after foaming each void transfers into a foam bubble. We showed that pore size, homogeneity, porosity, as well as morphology of the synthesized nanofoams are adjustable by the size and polydispersity of the polymer nanoparticles as well as the NF-CID parameters [2]. Following NF-CID, we were able to reduce the pore size of polystyrene nanofoams down to 80 nm. In a close cooperation with project **A5**, the produced nanofoams will be used as a template to synthesize PS/ZnO hybrid mesoporous material with $d \geq 25$ nm. A proof of principle has been recently reported using polystyrene nanofoams with a relatively large pore size ≈ 1 µm [2].

The second part of this study explores the influence of liquid confinement on the asymmetric Rh catalysis in a close cooperation with project **B3**. As a benchmark reaction, the 1,2-addition of Triphenylboroxine to *N*-tosylimine in the presence of a $[RhCl(C_2H_4)_2]_2$ catalyst and chiral diene ligands was chosen. To generate the liquid confinement, a microemulsion containing equal amounts of H_2O/KOH and toluene/reactants was formulated using *n*-octyl β-D-glucopyranoside (C_8G_1). Small-angle X-ray scattering (SAXS) proved that this organized reaction medium consists of water- and toluene-rich compartments with a domain size of 55 Å. Utilizing this self-organized reaction medium, we indeed found a markedly improved conversion and enantioselectivity as well as reaction rate (confirmed by kinetic studies) in case slightly polar diene ligands were used [3].

[1] R. Strey et al., *German Patent* Application 2010, *DE102010053064A1.*
[2] Y. Qawasmi et al., *Colloid Polym. Sci.* **2018**, *296*, 1805.
[3] M. Deimling et al., *Chem. Eur. J.* **2019**, *25*, 9464.

B1: Tetraaza-Ruthenium-Complexes supported on Azide-Modified SBA-15 Material for the Directed Hydrogen-Autotransfer Catalysis

Marina Fuhrer,[1] Pascal Eisele,[1] Franziska Bächtle[1], Bernd Plietker[1]

Institute of Organic Chemistry, University of Stuttgart, Stuttgart, 70569, Germany

Inspired by enzymes, the goal of the CRC 1333 is to evolve molecular heterogeneous catalysis with confinement effects as the key factor for selectivity. Hydrogen-autotransfer catalysis, olefin metathesis and asymmetric catalysis are the catalytic processes which shall be carried out in different mesoporous materials.

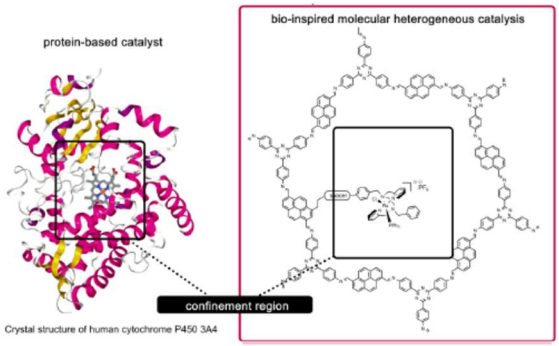

Figure 1: Bio-inspired molecular heterogeneous catalysis within the CRC.

In the Plietker Group we focus on hydrogen-autotransfer catalysis with our tetraaza-ruthenium-complexes [1]. The possibility to connect the complexes easily to the solid support via click-chemistry is given by integration of an alkyne functionality into the standard ligand.

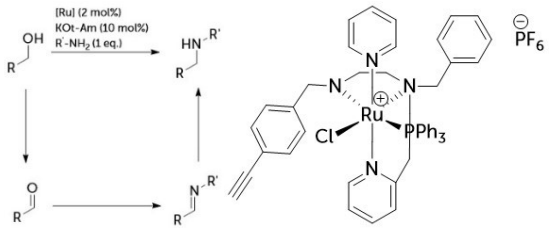

Figure 2: Scheme of the hydrogen-autotransfer catalysis and Ru-Complex with alkyne functionality for click chemistry.

To position the complexes in the center of the pores, it is necessary to use spacer molecules with different length and flexibility depending on the mesoporous materials. The first two spacer molecules have been synthesized via standard organic chemistry and they are distinguishable according their flexibility.
At the moment we are focusing on the azide-SBA-15 material as mesoporous material. The synthesis of this kind of materials has been published by T. D. Stack in 2012. [2] With this standard material in hand the challenging part begins: 1. Defunctionalization of the surface but not the pores, 2. Incorporation of the complex molecules into the pores, 3. Click-chemistry in the pores, 4. Detection of supported complex molecules in the pores.

[1] a) D. Weickmann et al., *Chem. Eur. J.* **2013**, *19*, 2741 2748
b) D. Weickmann et al., *ChemCatChem* **2013**, *5*, 2170-2173.
[2] J. Nakazawa et al., *JACS* **2012**, *134*, 2750-2759.

B2: *syn – anti* Interconversion of Molybdenum and Tungsten Alkylidene NHC Complexes

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Molybdenum and tungsten alkylidene complexes can exist as a *syn*-isomer (with the alkylidene pointing toward the imido-ligand) and an *anti*-isomer (with the alkylidene pointing away from the imido ligand).

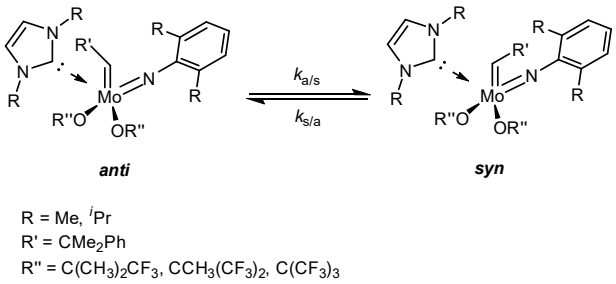

Figure 1: *syn-anti* interconversion of Molybdenum alkylidene NHC Complexes.

Whether the double bond, formed by a metathesis reaction is *cis* or *trans* depends on the coordination of the olefin and of the *syn* or *anti* configuration of the used catalyst. [1] It was shown that the polymer structure of ROMP derived polymers is dependent on the interconversion of those two forms of the catalyst, since the different isomers show different reactivities.[2] In most Schrock complexes and in our molybdenum and tungsten alkylidene NHC complexes the *syn*-form is the main isomer, but the *anti*-form can be generated by photolysis for Schrock Complexes [3] and for bisalkoxide alkylidene NHC complexes. For some other complexes, where the *anti* could not be generated by photolysis, it could be generated at lower temperatures in acetonitrile. After generating the *anti*-isomer the interconversion from *anti* to *syn* was examined by ^{1}H-NMR spectroscopy.

[1] R. R. Schrock, *Dalton Trans.* **2011**, *40*, 7484-7495
[2] M. M. Flook et al., *Organometallics* **2012,** *31*, 6231-6243
[3] (a) J. H. Oskam et al., *J. Am. Chem. Soc.* **1993**, *115*, 11831-11845
(b) J. H. Oskam et al., *J. Am. Chem. Soc.* **1992**, *114*, 7588-7590

B2: Macrocyclization in Confined Spaces: Olefin Metathesis Catalysts Immobilized on Tailored Mesoporous Silica

Felix Ziegler[1], Johannes Teske[1], Iris Elser[1], Wolfgang Frey[2], Michael R. Buchmeiser[1]

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Ring closing metathesis (RCM) of long chain dienes provides access to valuable macrocycles. However, state of the art methods require high dilution (5 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. [1-5] We envisioned that the fixation of an olefin metathesis catalyst in a confined space would result in the suppression of ADMET and might allow higher substrate concentrations. Therefore, a Grubbs-Hoveyda 2nd-generation catalyst derivative was immobilized on SBA-15 with varying pore sizes (48, 63 Å) via one of its NHC (*N*-heterocyclic carbene) wingtips.

Exclusive immobilization in the pores was achieved in a three-step treatment of commercially available SBA-15. The catalyst is then introduced by the silylation of the silanols in the mesopores with the trimethoxysilane group on the NHC.

Application of the different types of SBA-15 containing the catalyst **[Ru-48]**, **[Ru-63]** in the macrocyclization of different substrates revealed a clear correlation between pore size and the ratio of mono macrocyclization (**MMC**) to oligomerization (**O**).

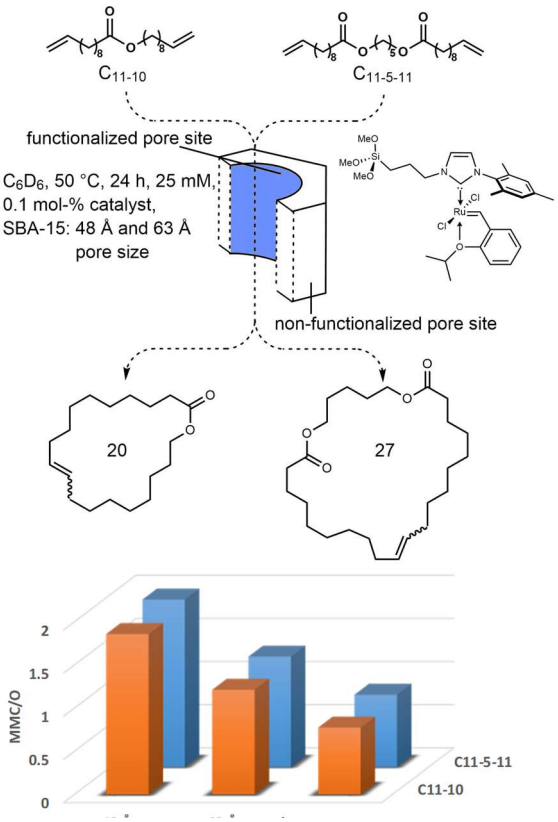

Figure 1: Application of the different types of silica containing the catalyst in the macrocyclization of substrates $\mathbf{C_{11\text{-}10}}$ and $\mathbf{C_{11\text{-}5\text{-}11}}$. Ratio of macrocycle formation to the competitive formation of oligomers with different SBA-15.

[Ru-48] provided the highest selectivity (up to 23% more MMC) compared to the homogenous catalyst at rather high concentrations of 25 mM. Additionally, the exemplary screening showed a huge impact of the substrate size, temperature and the catalyst loading on the ratio of macrocyclization to oligomerization.

[1] A. Gradillas et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 6086-6101
[2] J. C. Conrad et al., *J. Am. Chem. Soc.* **2007**, *129*, 1024-1025
[3] J. E. Jee et al., *J. Org. Chem.* **2013**, *78*, 3048-3056
[4] A. Sytniczuk et al., *J. Am. Chem. Soc.* **2018**, *140*, 8895–8901
[5] C. S. Higman et al., *J. Am. Chem. Soc.* **2018**, *140*, 1604-1607

B3: Synthesis of Clickable Chiral Bicyclo[3.3.0]octadiene Ligands and their Application in Asymmetric Rhodium Catalysis

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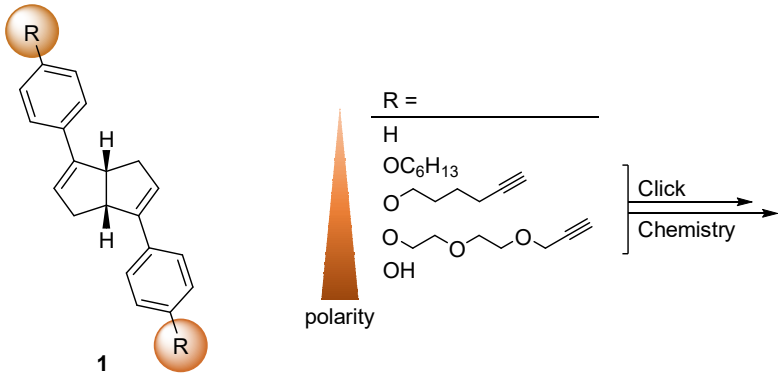
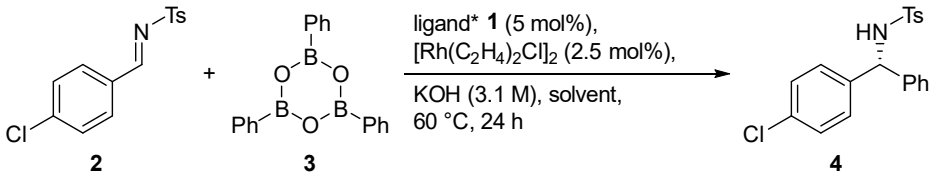
[2]*Institute of Physical Technology, University of Stuttgart, 70569 Stuttgart, Germany*

Microemulsions demonstrated to be a good alternative to conventional solvents in various homo-geneous metal catalysis reactions.[1] Due to their enormous internal interfacial area and miscibility of polar and nonpolar reactants, microemulsions can achieve increased reaction rates and higher yields.[2] However, there are only few examples of homogenous asymmetric catalysis in micro-emulsions,[3] which led us to the development of novel chiral bicyclo[3.3.0]octadiene ligands **1** of different polarities.[4] Due to their terminal alkyne groups, ligands can be further functionalized by click chemistry.



We tested this set of diene ligands in the rhodium catalyzed 1,2-addition of triphenylboroxine **3** to *N*-tosylimine **2** in an optimized microemulsion as reaction medium.[4] Experimental results on yield, chemo- and enantioselectivity have been underlined by temperature dependent kinetic studies. For comparison, reactions were also carried out under homogenous conditions.



Alkyne carrying ligands were clicked to azide functionalized surface materials like SBA-15 and dummy substances. Afterwards, clicked ligands have been tested in rhodium catalysis under homogenous conditions to check the influence of the newly formed triazole group.

[1] a) S. Serrano-Luginbühlet al., *Nat. Rev. Chem.* **2018**, *2*, 306–327
b) M. Schwarze et al., *Catal. Sci. Technol.* **2015**, *5*, 24–33.
[2] a) T. Sottmann et al., *J. Chem. Phys.* **1997**, *106*, 6483–6491
b) K. Holmberg, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 187–196.
[3] a) M. Schmidt et al., *ACS Omega* **2018**, *3*, 13355–13364
b) S. Handa et al., *Angew. Chem. Int. Ed.* **2014**, *53*, 10658–10662
Angew. Chem. **2014**, *126*, 10834–10838.
[4] M. Deimling et al., *Chem. Eur. J.* **2019**, *25*, 9464–9476.

B3: Chiral Norbornadiene Ligands for Rhodium Catalysis in Microemulsions and their Immobilization in Mesoporous Materials

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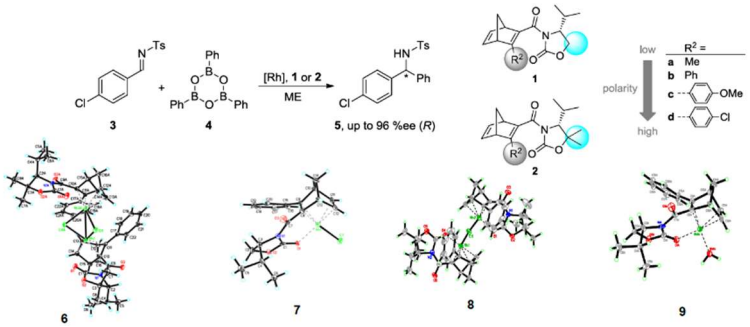
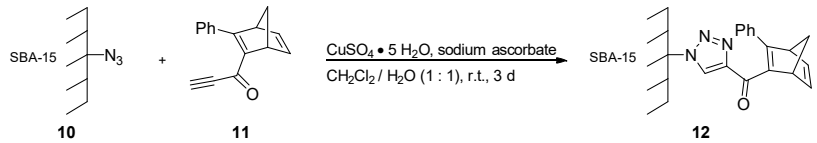
Due to improved solubility of reactants and mass transport, microemulsions (ME) have been used as reaction media for homogeneous metal catalysis.[1] Furthermore, microemulsions consist of nanostructures that might lead to confinement effects in catalysis.[2] Therefore, we investigated the influence of microemulsions on the rhodium-catalyzed 1,2-addition of triphenylboroxine **4** to *N*-tosyl imine **3** applying norbornadiene ligands **1** and **2** with different polarity and steric demand in cooperation with Sottmann´s group.[3] The use of microemulsions as reaction media markedly improved conversion as well as it changed enantioselectivity. Kinetic studies using ligand **1b** revealed that the reaction rate was significantly increased in microemulsions. Through X-ray crystal structures it was shown that the rhodium complexes **6** and **8** with norbornadiene **2b** formed rhodium dimers, whereas the rhodium complexes **7** and **9** with norbornadiene **1b** formed monomers leading to different enantioselectivities and yields in catalysis.



Scheme 1: Chiral norbornadiene ligands and rhodium complexes for the the rhodium-catalyzed 1,2-addition of triphenylboroxine **4** to *N*-tosyl imine **3.**

To investigate possible confinement effects in mesoporous materials, the clickable alkine-substituted norbornadiene ligand **11** was synthesized from the precursor **2b** and subsequently clicked with benzyl azide as a testing reagent. Since triazoles were successfully obtained, initial immobilization experiments with azide-functionalized non-porous silica material SBA-15 **10** were carried out in cooperation with Traa's group. In order to probe wheather the immobilization was successful, infrared spectroscopy was performed which revealed that the number of azide groups significantly decreased after the click reaction. Further investigations via solid-state NMR and catalysis experiments are in progress.



Scheme 2: Immobilization of the alkine substituted norbornadiene **11** on the azide-functionalized SBA-15 **10.**

[1] S. Serrano-Luginbühl et al., *Nat. Rev. Chem.* **2018,** *2*, 306–327.
[2] T. Sottmann et al., *Fundamentals of Interface and Colloid Science*, Vol. 5, **2005**, pp. 5.1–5.96.
[3] M. Deimling et al., *Chem. Eur. J.* **2019**, *40*, 9464–9476.

C1: Effect of Aluminum on adsorption and desorption of water and methanol on micro- and mesoporous solids

Zheng Li[1], Carolin Rieg[1],Michael Benz[1], Michael Dyballa[1], Michael Hunger[1]

[1]*Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany*

Adsorption and desorption of water as well as methanol on porous solids have been investigated by ^{1}H MAS NMR spectroscopy and thermogravimertric analysis (TGA). For microporous MFI zeolites, aluminum, cations and acidic OH groups (H^+) strongly increase the adsorption capacity of water by a factor of 9, while these sites have little effect on the methanol adsorption. Similarly, on mesoporous SBA-15, the adsorption capacity of water raises with increasing aluminium content. However, the aluminium modification leads to lower adsorption of methanol on SBA-15. After a 30-minute room-temperature desorption, the ^{1}H MAS NMR spectra changed remarkedly. Signals of hydronium ions and complexes of water at cations become visible. On microporous materials, the nature of water species is more diverse than on mesoporous meterials.

C1: New solid-state NMR probe molecules for characterization of noble metals on porous supports

Carolin Rieg[1], Zheng Li[1], Isabel Lorenz[1], Michael Hunger[1], Michael Dyballa[1]

[1]*Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany*

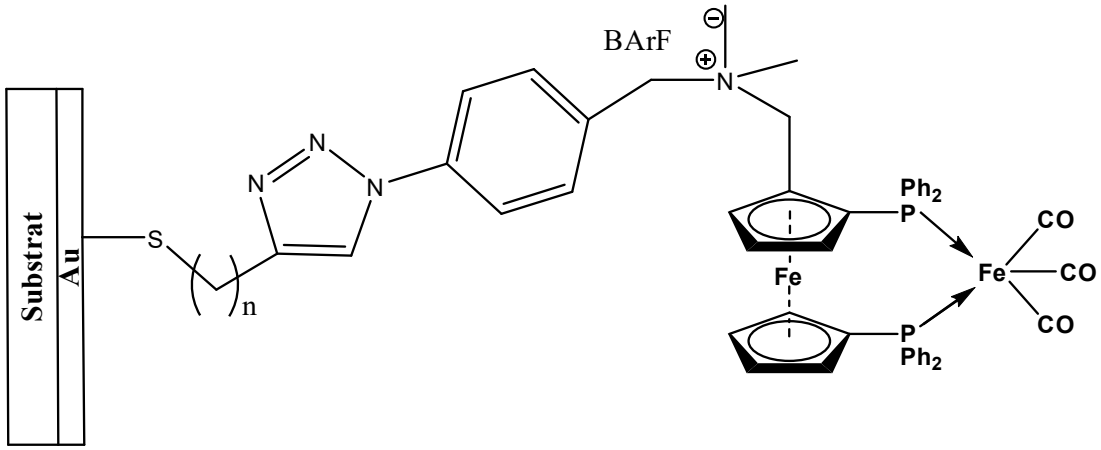
For industrial processes in heterogeneous catalysis information like acid strength (qualitative), distribution, steric location and concentration (quantitative) of the active centers are indispensable. Brønstedt and Lewis acid sites in solid acids like zeolites are detectable by use of i.e. trimethylphosphineoxide, ammonia or acetonitrile as molecular probes. Until now, no spectroscopic probe molecule exists for the study of metal centers inside the pores and at the outer surface of the porous materials. We demonstrated successfully that triphenylphosphine (TPP) is a useful molecular probe and tool for quantitatively characterizing the spatial distribution of noble metals (NM) or noble metal ions on porous supports. Additionally, new knowledge about using aryl- and alkylphosphines and their corresponding oxides is obtained. The complex formation between TPP and ruthenium, platinum and molybdenum to noble metal tetrakis(triphenylphosphine), $NM(PPh_3)_4$, on mesoporous SBA-15 was quantitatively observed by ^{31}P MAS NMR spectroscopy. These complexes have a molecular size of ca. 1.9 nm, so they can form in mesopores (3.5 to 4.5 nm), but not in the cages of Y-zeolites (0.72 and 1.14 nm), what we proved experimentally. Basic experiments about the reactivity of various probe molecules with noble metals and noble metal ions were done on silica. The preparation of the samples was made in the following way: the support was layered after heating (723 K for 12 hours) with TPP in nitrogen atmosphere in a rotor, then the mixture way heated at 363 K for 20 hours. For the solvent loading, we stirred mechanically the TPP and the porous material in dry toluene, and the solvent was evaporated in vacuum.

C2: Click-functionalization of (dppf)Fe(CO)$_3$

Marc Schnierle[1] Mario Winkler[2] Joris van Slageren[2], Mark R. Ringenberg[1]

[1]Institute of Inorganic Chemistry, [2]Institute of Physical Chemistry
Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart (Germany)

The compound, the (dppf)Fe(CO)$_3$ molecule (dppf = 1,1'-bis(diphenyl-phosphino)ferrocene), on which the presented work is based, was chosen because of its interesting properties. In preliminary work, this molecule was synthesized and studied spectroelectrically, spectroelectrochemically and structurally. Some interesting properties of the (dppf)Fe(CO)$_3$ are the formation of a quasi iron-iron bond and a coordination change of the ligands with the oxidation of the compound. [1]



The synthesis of the functionalized (dppf)Fe(CO)$_3$ derivative is based on *N,N*-dimethylaminomethylferrocene. The novel synthesized inter-mediates and complexes were analyzed electrochemically and spectroscopically (IR, NMR, CV). Furthermore, it is to be determined how the geometric and electronic structure of the system changes during the functionalization and immobilization.

[1] M. Ringenberg et al., *Inorg. Chem.* **2017**, *56*, 7501–7511

C2: The Electronic and Geometric Structure of Catalysts in Mesopores

Mario Winkler[1], Marc Schnierle[2], Mark Ringenberg[2], Joris van Slageren[1]

[1]Institute of Physical Chemistry, [2]Institute of Inorganic Chemistry
Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart (Germany)

In order to understand the behavior of a catalyst in a pore, one must be able to probe the chemical properties of the compound inside and outside of the pore. This is why the (dppf)Fe(CO)$_3$ catalyst was chosen as the system of interest. [1] It allows several spectroscopic techniques in its oxidised, paramagnetic form, such as EPR spectroscopy (revealing two isomers with S = 1/2 and $g \approx 2$), SQUID magnetometry (revealing an interaction between the two iron sites in the molecule), MCD spectroscopy (revealing purely C terms as are expected for paramagnetic compounds and no similarities of the oxidised form with the neutral compound or the precursor Ferrocenium), DFT calculations (confirming the assumption of unpaired electron density on the ferrocene iron site) and Mößbauer spectroscopy, which is yet to be performed in detail.

The incorporation of a simpler radical (4-Azido-TEMPO) into a COF (provided by project **A3**) [2] via click chemistry revealed an interaction of these radicals, leading to much different lineshapes and relaxation times of the magnetisation in pulsed EPR. The spin-spin and spin-lattice relaxation time of the immobilised radical is lower than that of the free TEMPO molecule by a factor of 1000 at 7 K. This is likely a result of the small distances between the paramagnetic centers and a resulting dipolar coupling.

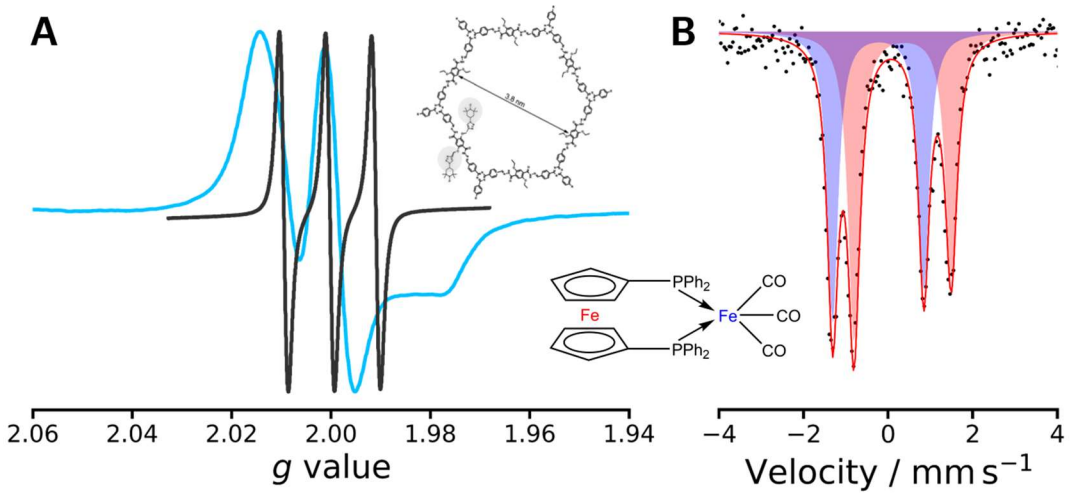


Figure 1: **A**: Room temperature X-Band EPR of the free 4-Azido-TEMPO (grey) and the immobilised radical in the COF (blue). The linewidth increases due to exchange broadening or motional averaging from nearby spins. [3] **B**: Mößbauer spectrum of the investigated catalyst (dppf)Fe(CO)$_3$ at room temperature clearly indicating two different iron sites with similar quadrupole splitting parameters but different isomer shifts resulting from varying *s*-electron densities at the nuclei.

[1] M. Ringenberg et al., *Inorg. Chem.* **2017**, *56*, 7501–7511
[2] L. Stegbauer et al., *Chem. Sci.* **2014**, *5*, 2789–2793
[3] B. K. Hughes et al., *J. Phys. Chem. Lett.* **2016**, *7*, 3660–3665

C3: High Resolution Tomography of Mesoscopic Pore Structures

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[1]*Institut für Materialwissenschaft, Heisenbergstraße 3, 70569 Stuttgart*

Atom Probe Tomography (APT) is a powerful technique for the measurement of solid materials. To expand APT to organic and biological materials like liquids and soft matter a new preparation protocol for the tip production out of frozen liquids was developed at our institute. Firstly, the wetting surface of the support wire is tailored by applying a tensile force to a tungsten wire under cryogenic temperatures, the cold support wire is then dipped into the frozen liquid such as octane or decane, frozen water is removed by freeze edging and a needle-shaped tip can be produced by milling with a focused ion beam (see figure 1A-C). Afterwards the tip out of the frozen liquid is measured by conventional laser-assisted APT (see figure 1D). This routine can most likely be applied to any liquid material such as microemulsions, containing nanostructured phases of different components such as sucrose, octane and surfactant polymers (project A7). By applying a 3D reconstruction to the measured APT data the individual nanostructured phases of the microemulsion will become visible for the very first time.

Moreover, by filling the nanopores of solid material such as silica with a contrasting liquid the mesoscopic pore structure can become visible in 3D, what would be quite beneficial for the optimization of the template structures that are produced in section A.

To achieve these ambitious goals a new hybrid instrument joining a focused ion beam microscope and an atom probe chamber was already built but still has to be brought to daily operation for a faster measurement routine of cryogenic samples.

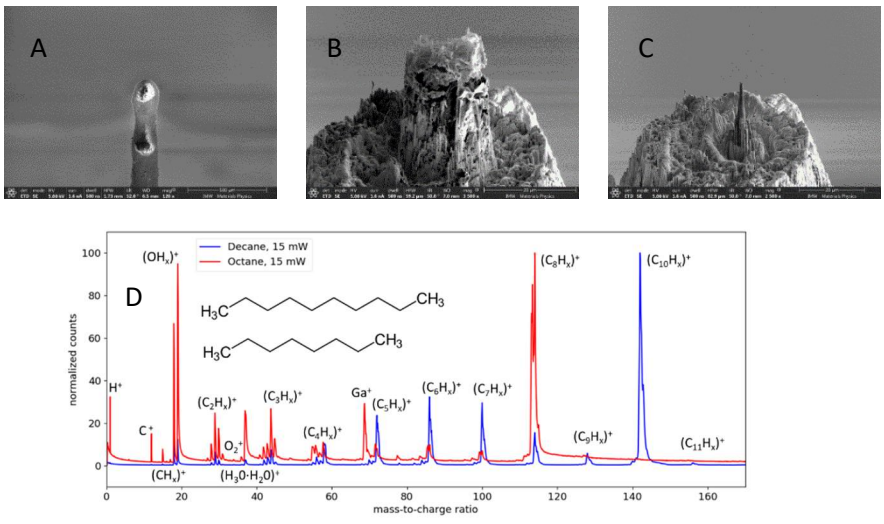

Figure 1: Cryo APT measurements of decane and octane. After dipping a tungsten wire into decane, shock freezing with liquid nitrogen and freeze edging, the frozen liquid remains on the tungsten wire (A) and by milling with a focused ion beam a needle-shaped tip can be produced (B, C). The resulting mass spectra of decane and octane tips are shown in D.

C3: Atom Probe Tomography of self-assembled Monolayers

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[1]*Institute for Material Science, Heisenbergstraße 3, 70569 Stuttgart*

This part of project **C3** focuses on the bonding of small molecules to the surface of the porous matrix and thus investigates the linkage of molecules to the pore wall. Therefore, simple model molecules which form by self-organization, so-called self-assembled monolayers (SAM), are investigated by atom probe tomography (APT). This technique excels at chemical sensitivity and provides furthermore three-dimensional spatial information of the probed samples.

Experiments are conducted by preparation of nanometer-sized metallic needles, which are cleaned by field-evaporation and then coated by dipping in the according solution of thiol-based SAMs for several hours. The resulting monolayer has a thickness of less than two nanometers and is analyzed by laser-assisted APT. The carbon chains break under the influence of the high electric fields and corresponding molecular fragments are detected by time-of-flight mass spectrometry. The reconstruction reveals an ordered evaporation sequence of the molecule chain down to the substrate and provides information of surface coverages of the SAMs.

The substrates will be extended to oxide materials like SiO_2, Al_2O_3 and others, which are of interest in this CRC and coated by monolayers containing silane and phosphonic acid head groups which bind to oxides.

In collaboration with **A5**, atom probe tips coated with APTES will used to bio-mineralize ZnO. This layer will be further functionalized with different SAMs and characterized with APT.

C4: Field Desorption of Organic Molecules

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Atom probe tomography (APT) is a promising technique which may allow the three dimensional reconstruction of materials with atomic resolution. This technique is currently being tested on self-assembled monolayers (SAMs) of organic molecules deposited on metal tips. A strong voltage is applied to the tip, resulting in fragmentation of the molecules in the electric field. The ionized fragments can be detected and the structure of the SAM on the tip reconstructed. [1]

APT is an established technique for investigating metallic structures, however, for organic molecules, the underlying mechanism, namely field desorption, is not yet fully understood. For this reason, the process of field desorption is simulated using density functional theory (DFT).

In the theoretical model, the external field is incrementally increased until the molecule breaks apart and the ionized fragments fly away in the direction of the electric field. We can observe, which bonds break at certain field strengths and how much charge the fragments are carrying.

The system is strongly simplified by reducing the model to a single molecular chain on a cluster of 10 metal atoms. Thereby surface effects and intermolecular interactions in the SAM are neglected. Nevertheless, this still provides us with enough insight to lay the groundwork for further calculations.

[1] A. Stoffers et al., *Langmuir* **2012**, *28*, 56-59

C4: Density Functional Theory and Forcefield Parametrization for Covalent Organic Frameworks

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Covalent organic frameworks (COFs) are an emerging class of crystalline polymers and are used to construct porous structures. Within the framework of the CRC 1333 they are intended to act as possible porous environment for catalytic reactions. In order to form porous structures a stacking of several COF layers is necessary. The stacking behaviour is predominantly influenced by the Van-der-Waals interaction between layers. This behaviour manifests itself in relative horizontal and vertical shifts of the layers against each other. The resulting interlayer distances as well as the stacking behaviour between layers are of major interest for experimental applications. The COFs are described with Density Functional Theory (DFT) to obtain further insight into underlying interaction effects as well as their temperature stability. As the investigated COFs are periodic structures with hexagonal symmetry, they can be described via their respective unit cell. For obtaining meaningful descriptions the application of periodic boundary conditions and the use of plane wave DFT-Methods is necessary. With these models we can obtain structural information and determine effects that influence the preference of certain stacking types, interlayer distance, pore size as well as overall structural stability. The obtained structures and informations are then used to find the most suitable COF for the task at hand, which is then used as reference to parametrize a force field upon the DFT results, to reproduce the quantum mechanical behaviour within the classical picture. This is of main interest as the COF is intended to act as environment for the catalytic reaction mechanisms that are to be investigated inside the pore structure, to determine changes in the reaction profile inside the COF environment. For this purpose a QM/MM framework is used, where the catalyst is treated quantum mechanically and the COF classically.

C5: Atomistic Simulations and Classical Density Functional Theory

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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 and the adsorbent-adsorbate interactions are needed. Due to the possibility of conducting unphysical moves Monte Carlo Simulations (MC) are the tool of choice to study adsorption behavior. One saves computational effort equilibrating and sampling the system sufficiently. 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 COFs. [1]

Classical Density Functional Theory (DFT) is another method which allows to derive the previously mentioned properties. The density profile is predicted by minimizing the grand potential. Excellent agreement between the two methods can be shown [2]. DFT simulations are much less computational expensive and allow to conduct a larger amount of simulations to obtain e.g. pore size distributions.

Besides the mentioned above realistic structures model systems can be built and used to study the isolated impact of fluid or solid properties on adsorption properties. One can investigate e.g. slip effects in COFs or chemical heterogeneities of surfaces.

Results are presented for adsorption in COFs as well as for density profiles of model systems.

[1] A. Sharma et al. *CrystEngComm,* **2017**, *19*, 69506963
[2] E. Sauer et al., *Langmuir,* **2019**, *35*, 11690-11701

C6: Structural characteristics of oxide surfaces from quantum- mechanical calculations

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Oxide surfaces are studied here by means of quantum-mechanical calculations implementing the density functional theory. We investigate different surfaces made of ZnO, TiO_2, and SiO_2. These are analyzed with respect to their structure and morphology. Through our simulations, we also assess their stability with respect to the different crystallographic planes taken to cut the surface from the bulk crystal. Our results underline the characteristics in their electronic properties, such as the electronic density of states and their band structure. These are compared to their bulk counterparts and show distinct features. In the end, we will discuss the relevance of these oxide surfaces in accommodating an organic layer to form inorganic/organic hybrid materials.

C6: Statistical Insights into Olefin-Metathesis Catalysis in Nanotubes via Coarse-Grained Particle-Based Simulations

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We construct a particle-based method to model the olefine-metatesis catalytic reaction. The core feature of this method is the creation and destruction of bonds between a catalyst particle and other reactant particles. An example on how this method operates is shown in figure 1. This models certainly lacks many chemical details, but is very fast and has the advantage that we are able to run long simulations to get statistical insight into the outcome of these reactions.

With this model in hand we investigate the influence of nanopore geometries on olefin metathesis. The system we have chosen to look at consists of a solution of dienes, which can either undergo an ring closing metathesis or polymerization, depending on whether the tail of an attached diene or another diene hits the catalyst first. For those two reaction types we investigate the dependencies of the density and the length of the dienes. To check for the influence of confinement we perform each simulation twice, once insight a nanopore and once without a nanopore.

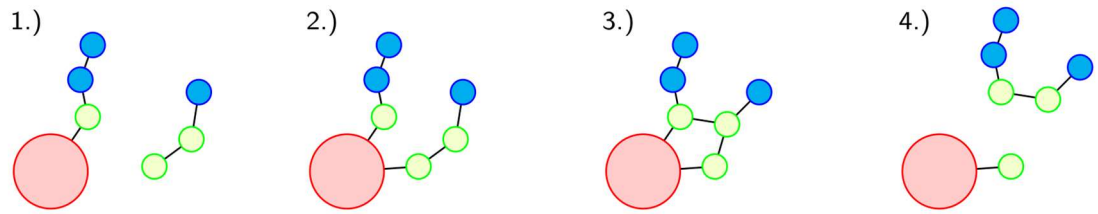

Figure 1: Reaction scheme of the model. The catalyst is illustrated in green, the normal particles in blue, and the particles that can attach to the catalyst are depicted in green. 1.) A free particle chain approaches the catalyst. 2.) A bond between the catalyst and the colliding particle is created. 3.) A bond is formed between the chains. 4.) Some bonds are being broken, which leads to a new particle chain.

S1: X-ray absorption 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**, X-ray 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].

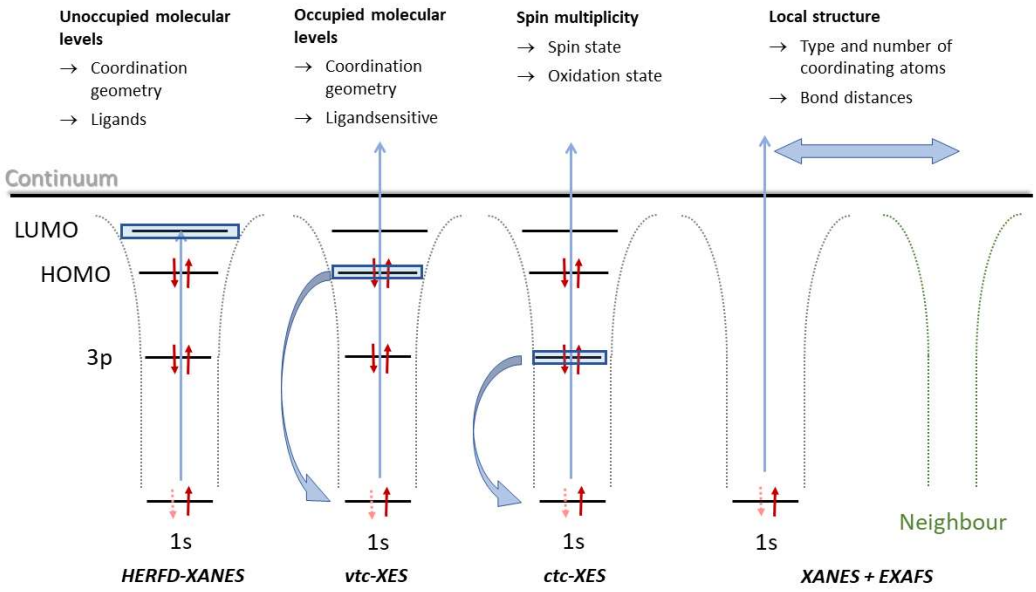

Figure 1: Hard X-ray methods and provided information for the example of K-edge spectroscopy. [1].

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