2.3 Department of Heterogeneous Catalysis

Director:
Ferdi Schüth (born 1960)

Further group leaders:

Frank Marlow (born 1960)

Gonzalo Prieto (born 1981)

group leader since 2015

Wolfgang Schmidt (born 1962)

Harun Tüysüz (born 1978)

Claudia Weidenthaler (born in 1965)

Curriculum Vitae: Ferdi Schüth

1960	Born in Allagen (now Warstein), Germany
1978-84	Chemistry studies at the Westfälische Wilhelms-Universität Münster, Diploma October 1984
1983-88	Law Studies at the Westfälische Wilhelms-Universität Münster, First State Examination February 1989
1984-88	Doctoral studies in the group of E. Wicke, Institute of Physical Chemistry, Münster, Dr. rer. nat. June 1988
1988-89	Post-doc at the Department of Chemical Engineering and Materials Science, University of Minnesota, USA, L. D. Schmidt
1989-95	Wissenschaftlicher Assistent (Assistant Professor) at the Institute of Inorganic and Analytical Chemistry of the Universität Mainz, K. Unger, Habilitation February 1995
1993	Visiting Assistant Professor at the Department of Chemistry, University of California at Santa Barbara, USA, G. D. Stucky
1995-98	Full Professor of Inorganic Chemistry at the Johann-Wolfgang-Goethe Universtität Frankfurt
1998-	Scientific Member of the Max Planck Society and Director at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr

Awards and Honors

1989	Award for outstanding Ph.D. thesis
1991	Boehringer-Ingelheim Research Award
2001	Award des Stifterverbandes für die Deutsche Wissenschaft
2003	Gottfried Wilhelm Leibniz Award of the Deutsche Forschungsgemeinschaft
2007	Honorary Professor of Dalian University of Technology, China
2008	Elected member of German Academy of Science Leopoldina
2009	Guest Professor Beijing University, China
2009	European Research Council Advanced Grant
2010	Heisenberg-Medaille of the Alexander von Humboldt Foundation
2010	Elected member of the Nordrhein-Westfälische Akademie der Wissenschaften und der Künste
2010	Nominated for the Deutscher Zukunftspreis 2010
2011	Ruhrpreis für Wissenschaft und Kunst (Ruhr Award for Science and Arts)

2011	Wöhler-Award for resource-saving processes
2011	Hamburger Wissenschaftspreis (Hamburg Award for Science)
2012	Wilhelm-Klemm-Preis of the GDCh
2013	Chemical-Engineering-Medal of the ETH Zürich
2014	Carl Friedrich von Weizsäcker-Award
2016	Honorary doctorate of TU Munich

Other Activities / Committees (only current)

1996-	Member of the Editorial Board, *Microporous Materials*
1998-	Member of the Editorial Board, *Advanced Materials*
2000-	Member of the Dechema Board of Governors
2003-	Member of the Editorial Board “QSAR-Combinatorial Science”
2005-	Chairman of the Investment Committee “Life Science, Materials and Energy” of the German High-Tech Fund
2005-	Member of the Editorial Advisory Board, *Chemical Engineering & Technology*
2006-	Editor, *Chemistry of Materials*
2006-	Member of the Advisory Board, *Chemistry–An Asian Journal*
2007-	Member of the Editorial Board, *Advances in Catalysis*
2007-	Member of the Hochschulrat, University Duisburg-Essen
2009-	Vice-Chairman of Dechema
2010-	Member of the Trustees of the Federal Institute of Materials Testing and Research (BAM)
2011-	Member of the Board of Trustees of the Award “Otto-Bayer-Preis”
2012-	Member of the selection committee of the “Deutscher Zukunftspreis” (Future Award of the German President)
2013-	Chairman of the selection committee of the “Deutscher Zukunftspreis”
2014-	Vice President of the Max-Planck-Society in Munich
2016-	Chairman of the Scientific Commission of Lower Saxony

Department of Heterogeneous Catalysis

The situation in the department in the reporting period was strongly affected by the election of Ferdi Schüth to the office of vice president of the Max-Planck-Society. While this is technically an honorary position – only the office of president is a full-time position in the MPS – it requires in fact approximately 75 % of the time. The group of the department head was consequently downsized to some extent, and each new Ph.D. student of Ferdi Schüth is assigned to a group leader as second supervisor. Nevertheless, the office requires substantial periods of absence which reduces the possibility of personal interactions with the members of the department. However, due to the fact that the group and the department was always organized in a rather independent manner, relying strongly on interactions between the members, and the quality of the senior scientists in the department, the overall performance currently does not seem to have substantially suffered. Also efforts to secure third-party funding have been taken over to a large extent by the group leaders, so that also here the decreasing time resources of the department head are essentially compensated.

As in previous reporting periods, the department of Heterogeneous Catalysis has seen change in the personnel situation over the last three years, not only on the level of post-docs and Ph.D. students, where it is natural, but also on the level of the group leaders. The positions of some of the group leaders are non-permanent, so that they contribute to the scientific profile of the Institute for limited periods only, and then find new challenges at other institutions. This allows to bring in new ideas with new scientists from outside of the institute. Continuity of the work, on the other hand, is ascertained by the director of the department (F. Schüth) and few senior scientists on permanent positions (F. Marlow, W. Schmidt, C. Weidenthaler, M. Felderhoff). Compared to the other departments of the Institute, the number of senior scientists is somewhat higher, which is due to the fact, that this is the only department focused on solids, which requires to maintain a range of different expertise specifically for the department alone.

During the reporting period, Roberto Rinaldi, who had pursued a vigorous research program in biomass conversion, left the institute for a faculty position at Imperial College. Part of the research activities in this field will be continued in the Schüth group, especially those on sugar and on bio-oil conversion, while the activities in lignin conversion are to a large extent discontinued, since they will be a major thrust of the Rinaldi group in London. Part of the members of Rinaldi-group stayed at the Institute in order to finish their projects, the last students and post-docs left the department early in 2017.

The successor of Roberto Rinaldi as group leader is Gonzalo Prieto. He had joined the institute as post-doc coming from the group of Krijn de Jong, and due to the excellent performance was promoted to a group leader position in 2015, initially financed by a Humboldt-Fellowship, followed by a Marie-Curie Fellowship and now on a senior scientist position of the Institute. Gonzalo Prieto has initiated a strong research program on the conversion of small molecules in energy relevant reactions, supplemented by the knowledge-based synthesis of structured catalysts and their analysis by advanced electron microscopy techniques.

In addition to the move of Roberto Rinaldi to Imperial College, also several other scientists were promoted to faculty positions at leading institutions. Ryan Wang, who was a post-doc in the department, accepted an offer to join the faculty of University College London, and Dong Gu and Guanghui Wang received offers for professor positions at the Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Science and the Wuhan University in China, respectively.

The research activities of the department continue to be centered on the synthesis of nanostructured catalysts and their use in different catalytic reactions, most of these reactions being relevant in energy conversion processes. The different groups of the department work together on different aspects of this overall thrust, to a large extent in joint projects. The group of Ferdi Schüth is focused on the synthesis of nanostructured catalysts based on polymeric supports, in which the distribution of the active material is controlled on the level of nanometers. The materials are applied as sinter-stable electrocatalysts or in biomass conversion reactions. In addition, the group pursues research on unusual catalytic problems, i.e. in methane activation in oleum to result in methylbisulfate, or in the conversion of acetylene to value-added products. The group is also interested in the fundamentals of solids formation, where there is a close interaction with the group of Wolfgang Schmidt, whose activities are directed to the use of zeolites in different applications and to the understanding of zeolite formation on the molecular level. The formation of materials on the atomic scale can only be studied by a coordinated effort, bringing together complementary experimental techniques, which are ideally used in-situ. Here the group of Claudia Weidenthaler is instrumental in developing new in-situ X-ray diffraction methods for use in the department. The thrust of the group is on the methodologies, but the examples to which the methods are applied are those which are relevant also for the other groups of the department. A prominent example for this interaction is the joint BMBF-funded project which Claudia Weidenthaler has won together with Michael Felderhoff. In this project, novel approaches towards hydrogen storage in complex hydrides are studied, and the in-situ analysis of the hydrogen adsorption/desorption processes are instrumental for the knowledge-based improvement of the systems. Hydrogen storage is one aspect of the research of Michael Felderhoff, but the complex hydrides can also be used for heat storage at different temperature levels. Heat storage is an important element in coupling the different sectors in our energy system, and thus a substantial fraction of the activities of the Felderhoff-group are directed at the practical implementation of hydrides as heat storage materials. The research focus of the Prieto group has already been described above: his team controls the active metal distribution in nanostructured materials in order to create the optimum catalyst for specific reactions, and these catalysts are then used for energy relevant reactions involving small molecules, such as in the coupling of hydrocracking/Fischer-Tropsch reactions. Harun Tüysüz and even more so Frank Marlow complement the activities of the department in using nanostructured materials for catalysis, but also especially for use in solar cells and in photo- and electrochemical reactions, where the use of such well-defined materials and careful analysis helps in understanding the fundamentals of these important application fields of nanostructured materials. Highlights of the research activities of the different groups are given further down in this book in the reports on the different research activities.

The analytical capabilities of the department were substantially extended by the acquisition of the new STEM Hitachi HD-2700 with a point-to-point resolution of 0.4 nm, but more importantly EDX analytical capabilities at a resolution of a few nm, depending on the sample. A joint Ph.D. student of Christian Lehmann and Ferdi Schüth is exploring the limits of the possibilities which this new instrument brings.

As can clearly be seen from the list of publications, there are many joint activities within the department and within the Institute. Beyond this, the department is linked to other groups world-wide in various ways, be it by joint projects, such as the Cascatbel EU-project or a project funded by the ministry of economy with five partners from academia and industry, by exchange visits of students and post-docs with many laboratories world-wide, including UC London, DTU Lyngby, or University of Wisconsin, or with guest professorships or named lectures, such as at Dalian University of Technology, UC Berkeley or Shandong University. On the German level, the involvement of the department in two Clusters of Excellence (CoE), funded in the framework of the German Excellence Initiative, should be mentioned. One of these clusters in centered at RWTH Aachen, with a focus on fuels from biomass (Roberto Rinaldi and Ferdi Schüth), the second one is located at Bochum University and is directed towards the understanding of solvation effects (Harun Tüysüz and Ferdi Schüth). Bilateral cooperations were also important in advancing the research activities of the department, which include the one with Osamu Terasaki (Stockholm and KAIST), Brad Chmelka (UCSB), Ryan Wang (UC London), and Soren Kegnaes (DTU Lyngby), amongst others. The department members are also active in teaching in the neighbouring universities, where Ferdi Schüth, Frank Marlow, Gonzalo Prieto, Harun Tüysüz, and Claudia Weidenthaler teach a number of different classes.

The research activities of the members of the department have also been acknowledged by a number of awards and academic distinctions, such as the Habilitation of Claudia Weidenthaler (2015) and Harun Tüysüz (2016), the Carl-Friederich-von-Weizsäcker Preis of the German Academy of Science, an honorary doctorate of TU München and the Mutterthies Lecture of UC Berkeley for Ferdi Schüth, guest professorships for Claudia Weidenthaler and Wolfgang Schmidt at Shandong University, or the Jochen-Block award of the German Catalysis Society for Harun Tüysüz. Moreover, Wolfgang Schmidt is editor-in-chief of Microporous and Mesoporous Materials, the key journal for porous materials research, and Ferdi Schüth is editor of Chemistry of Materials.

Also the third party funding activities were substantial. During the reporting period, Ferdi Schüth completed his ERC Advanced Grant project, Roberto Rinaldi the AvH Sofja Kovalevskaja Award. Moreover, several DFG-projects, BMBF, BMWi, AIF, and industry projects were pursued during the reporting period; in addition, a number of Alexander-von-Humboldt fellows were active in the department. This helps to expand the scope of the activities which would be somewhat more limited if only the Institute resources were available.

2.3.1 Research Area "High Surface Area Materials"

(F. Schüth)

Involved: P. Bazula, A. Pommerin, H. Bongard, M. Dierks, J. Engelhardt, D. Gu, I. Lim, V. Nese, A. Padovani, C. Pichler, F. Richter, B. Spliethoff, F. Wang, G. H. Wang, B. Zibrowius

Objective: The synthesis and study of high surface area and porous materials is a research theme which is pursued in the group for more than 20 year. The focus of the development is on oxides and carbons, and this research area has strong overlap with the other fields of research of the group, since many of the materials produced later find applications in catalysis or other fields. Templating, be it hard or soft templating, is the main method for the production of this class of solids, but the work is not restricted to it, but also relies on other methods, if they appear suitable. Also the group of Wolfgang Schmidt and Harun Tüysüz are active in the development of porous solids for specific applications, and there is fruitful collaboration between the different groups in the department, resulting sometimes in joint publications, but each group also pursues its individual research topics.

Results: The most spectacular success during the reporting period was certainly the development of the surface casting method for the synthesis of high surface area and ordered porous oxides[22]. Surface casting, i.e. the coating of a template with a very thin layer of another material with subsequent removal of the mold has so far only been successful in the case of carbon by a method developed by Ryong Ryoo in 2001, which could thus be obtained in the form of the hexagonal array structure of carbon tubes called CMK-5. In spite of many attempts, this method could not be extended to compositions other than carbons. Analysis of the synthesis process pointed towards insufficient interaction between the mold oxide and the material to be cast, resulting in the formation of particles in the pores instead of a surface coating. The lack of silanols on the surface of the template silica was identified as the reason for this insufficient interaction. Based on this, a mild, non-thermal template removal/surface activation process, relying on treatment with HNO_3/H_2O_2 at 80°C, was found to be suitable to induce selective surface coating of the silica template with a broad range of different materials. Using these templates, zirconia and iron oxide could be produced with a structure similar to CMK-5, although not quite as perfect. Various oxides could be obtained from mesocellular foams in a foam-like structure themselves. Important for practical applications, amorphous, high surface area silica gels could also be used as molds, resulting in very high surface area oxides. Several examples are shown in Fig. 1. Irrespective of the template used, the typical surface areas of the surface cast oxides exceed those of oxides obtained by hard templating by a factor of two to three, and surface areas on the order of 300-400 m^2/g are regularly achieved even for high density oxides, such as zirconia. Incidentally, the functionalization of the silica surface also improves the casting of polymers, and thus, CMK-5 with very high structural perfection can be obtained.

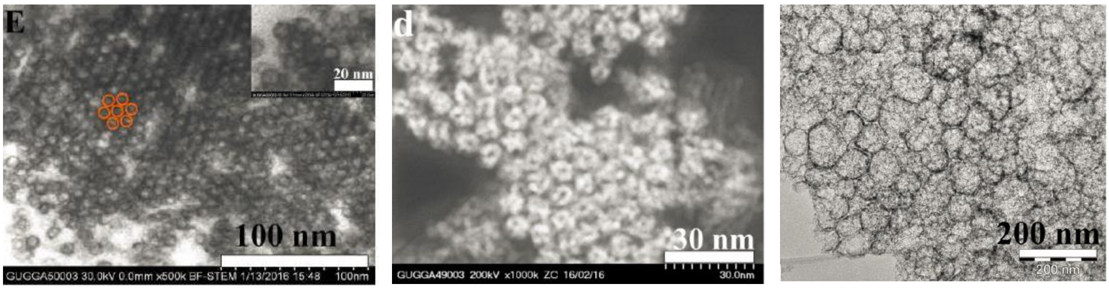


Fig. 1: TEM images of different surface cast oxides. Tubular ZrO_2 with a surface area of approximately 380 m^2/g (left); tubular Fe_2O_3 with a surface area of approximately 300 m^2/g (middle); mesocelluar TiO_2 with a surface area of approximately 250 m^2/g (right).

The oxides produced by the surface casting process consist of very small, connected oxide nanoparticles, which, based on TEM and XRD observations have sizes on the order of only a few nanometers, depending on thermal treatment temperatures. Also, the crystalline structure is sometimes unusual: zirconia is obtained as the cubic polymorph, which typically requires high temperature treatment. Whether this is due to residual silicon in the framework or the small primary particle sizes is currently unclear. The materials produced by the surface casting process are currently studied for different applications.

The nanocasting approach has also been used in its more conventional form of bulk casting for the synthesis of different oxides for specific catalytic applications. Casting of different cobalt-based materials with controlled doping has been used to identify the active sites in such catalysts for low temperature CO-oxidation[27]. In these studies, also materials consisting predominantly of Co^{2+} were found to be highly active, but surface oxidation of cobalt in octahedral sites was found to be responsible for high activity. If only tetrahedral cobalt sites were exposed to the surface, oxidation was found to be more difficult so that the resulting catalysts only showed moderate CO-oxidation activity. Similarly, a series of different manganese oxide based catalysts were produced by nanocasting[51]. Onto these solids, gold nanoparticles, produced by colloidal deposition, were placed and the resulting catalysts were studied again in CO-oxidation. The catalysts produced are the most active ones so far reported in literature for this reaction, and surprisingly, it was not Mn_2O_3, which so far was assumed to be the best support material, but the MnO_2 based system.

Nanocasting is also of high relevance in the production of systems for electrochemical applications. Nanocast carbon, loaded with Co_3O_4 at high loading levels was found to be an excellent electrode for lithium ion batteries[31], and the nanocasting synthesis of antimony-tin-oxide is currently used for the production of stable electrodes for the oxygen evolution reaction in the framework of MaxNet Energy.

While most of the synthetic activities directed at the production of high surface area materials rely on nanocasting and soft templating, another method recently implemented in cooperation with Duisburg-Essen University was found to be well suited for the high volume production of acidic high surface area carbon materials, i.e. pyrolysis in a continuous process[40]. Nebulizing a solution of sucrose and sulfuric acid directly led to the formation of acidic carbon materials after passing the aerosol through an oven at temperatures between 400 and 800°C with a residence time of 2 seconds. If salts were added to the solution, salt templating led to the development of a pronounced mesopore system, and materials with surface areas of around 500 m^2/g and acid site concentrations close to 2 mmol/g were obtained. The performance of the catalysts in fructose dehydration and inulin hydrolysis was comparable to commercial sulfonated resin catalysts, but the carbons have higher thermal stability and are easy to produce. Fig. 2 shows a TEM of a product synthesized in the presence of salt, where the mesopores are clearly visible, and the performance of different catalysts, including reference systems, in inulin hydrolysis.

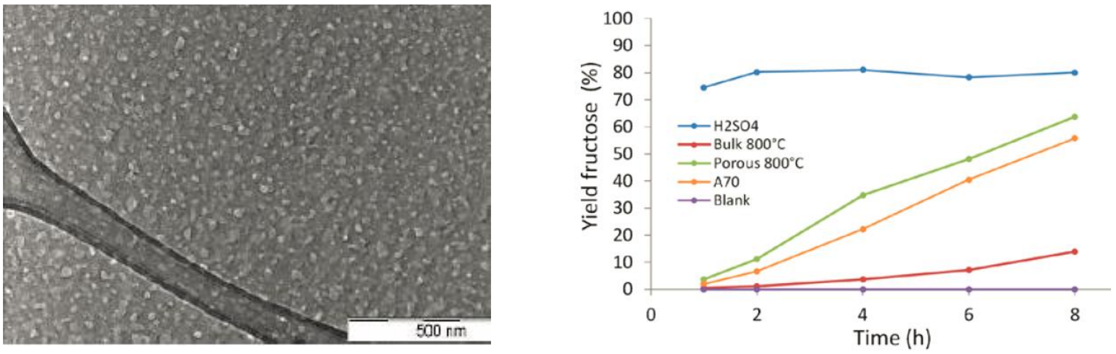


Fig. 2: TEM image of a sulfonated carbon obtained by spray pyrolysis. The white features are the pores created by salt templating (left); catalytic performance of such carbons in the hydrolysis of inulin, together with performance of reference catalysts; bulk 800°C is a catalyst obtained by pyrolysis at 800°C without salt, porous 800°C is the material pyrolized in presence of salt under otherwise identical conditions, A70 is Amberlyst A70, which was the most active one among three tested Amberlyst types (right).

In this research area also other high surface area materials, such as polymers, carbides, and oxides, were developed. Most syntheses relied on templating approaches, but also hydrothermal methods were used, as in the case of manganese oxides. Most of the resulting solids were used in biomass conversion reactions, such as for the hydrodeoxygenation of bio-oils, and they will therefore be discussed in the description of that research field.

Future directions: Work on high surface area materials belongs to the core activities of the department and has a cross-sectional quality, since many of the developed materials are used in other projects, either directly as catalysts, as catalyst supports for specific reactions or as starting materials for the preparation of nanoengineered materials. Therefore, work in this research area will continue in the future at least at the level as in the reporting period. In the last report, a shift away from ordered mesoporous materials was expected, since this field appeared to have reached a high level of maturity. However, with the successful development of the surface casting approach the research has taken a new turn, and therefore, surface casting will be an important research topic for the next years. The other systems will be continually developed further and used more as routine tools for the production of catalysts for specific applications.

Publications resulting from this research area: 9, 10, 19, 25, 26, 27, 28, 31, 33, 40, 44, 45, 49, 51, 52

External Funding: ERC, IMPRS SURMAT, EU Cascatbel

Cooperations: A. Fürstner, C. Lehmann, W. Schmidt, H. Tüysüz, C. Weidenthaler (Mülheim); W. Lubitz (Mülheim); A.H. Lu, W.C. Li (Dalian, CN); D.Y. Zhao (Shanghai, CN), D. Serrano (Madrid, ES), A. Lappas (Thessaloniki, GR); O. Terasaki (Stockholm, SE)

2.3.2 Research Area "Nanoengineered Catalysts"

(F. Schüth)

Involved: H. Bongard, N. Duyckaerts, D. C. Galeano-Nunez, D. Gu, D. Jalalpoor, J. Knossalla, S. Mezzavilla, C. Ochoa, B. Passas-Lagos, N. Pfänder, B. Spliethoff, A. C. Swertz, T. Trotus, J. vom Stein, G.H. Wang, F. Wang

Objective: The structuring of solid catalysts on the scale of nanometers and below is a continuing theme in the research of the department. If catalysts are synthesized in a controlled manner on this scale, they can be tuned towards specific applications. This research area thus tries to develop new and improve known methods for the nanostructuring of solid catalysts on the one hand, and on the other hand to apply the resulting catalysts for specific reactions. The synthetic approaches rely on a number of different methods, including nanocasting, colloidal deposition, and sol-gel chemistry. The synthetic work is complemented by different analytical methods, most notably and importantly electron microscopy.

Results: The development of nanoengineered catalysts was pursued predominantly in two different directions, i.e. the synthesis of hollow graphitic shell-based electrocatalysts, and different types of supported catalysts on the basis of polymers of the resorcinol-formaldehyde type and carbons derived from these polymers. Some other systems were studied as well, such as gold on manganese oxides which were synthesized by colloidal deposition. However, these systems will not be treated here in detail, since related systems have been the subject of extensive descriptions in previous reports.

The previous work on platinum-based fuel cell catalysts has been extended to different kinds of alloy catalysts[3,56]. In addition, the approach which had been used for the synthesis of the first generation of hollow shells is not suitable for the production of higher amounts. These, however, had been requested by several industrial companies who were interested in testing the catalysts in single cell measurements. Therefore, the synthesis was modified in order to provide scalable production routes[30,38,50]. Moreover, non-hollow reference catalysts have been synthesized in order to elucidate the origin of the good performance of the fuel cell catalysts.

Alloying of platinum is known to result in improved electrocatalytic performance. However, the production of alloys typically requires high temperature treatment which leads to growth of particles, with corresponding loss in electrocatalytic activity. This growth can be prevented by the “confined space alloying” approach, which was developed on the basis of the hollow graphitic spheres[3]. The alloying in the approximately 5 nm sized void in the shells of the hollow shell material restricts the growth of the forming alloy particles, so that the particle sizes remain around 4-5 nm. This in turn results in highly active electrocatalysts with approximately 2.5 times higher specific activity as the pure platinum catalyst (Fig. 1). A similar material, also with improved activity as compared to pure platinum, was obtained with platinum-cobalt alloys. The materials have extensively been studied with respect to structure, and especially concerning the leaching behavior under different aging conditions.

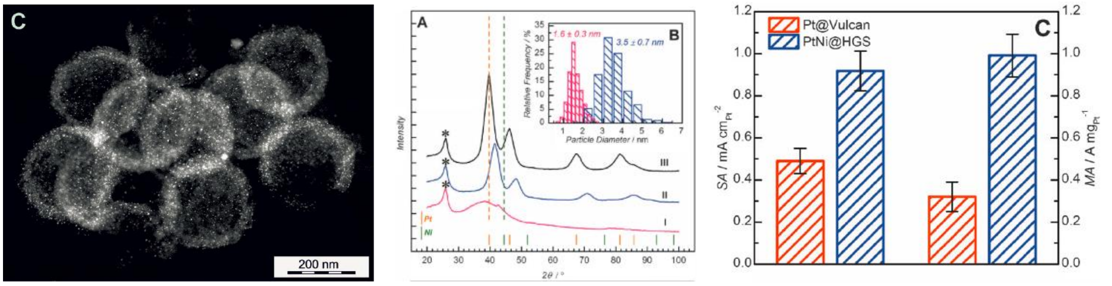


Fig. 1: PtNi loaded hollow graphitic spheres (left); XRD patterns of PtNi loaded hollow graphitic spheres (middle) after reduction (I), after high temperature treatment (II) and Pt/HGS for comparison (III). Area and weight normalized activity of Pt/Vulcan and PtNi/HGS (right).

The catalysts require several hundred redox cycles in order to remove the carbon layer formed during high temperature treatment. This is impractical in real fuel cell applications. Thus, alternatives have been investigated and finally, ozone treatment has been identified as a viable pathway[38]. Also the synthesis of the hollow shell substrate has been simplified, both by continuous synthesis in a tubular reactor and by a one-step synthesis of the solid core and the hollow shell[50]. Interestingly, a material in form of a solid sphere with otherwise identical textural properties performs equally well in rotating disc electrode measurements, but is inferior in single cell experiments. This implies either different mass transfer properties or different penetration by the Nafion ionomer.

The precursor for the hollow sphere materials is a polymer which is infiltrated into the pores of a silica hard template. Under suitable conditions, polymers can also be obtained with highly defined porosity and mesostructured in the absence of hard templates, but using surfactants instead. Resorcinol-formaldehyde-based resins have been developed as a highly versatile platform for the synthesis of different nanostructured catalysts, which are highly active and selective for different reactions. Conceptually, the resins are synthesized from precursors which contain ion exchange groups. The ion exchange sites can be used to anchor metal precursors in the polymer, and these precursors are converted to metals, alloys, or oxides in a subsequent thermal treatment step. Examples for precursors with ion exchange groups are 2,4-dihydroxybenzoic acid or 3-aminophenol. The crosslinking in these resins occurs between the hydroxygroups and the formaldehyde, while the carboxylic acid or amine functionality provide the ion exchange functionality. These polymers have proven to be highly suitable for the synthesis of different catalytic materials. Various metals and metal alloys could be deposited in this way in the form of very highly dispersed nanoparticles in these resins and the carbons obtained after thermal treatment; with a somewhat modified synthesis protocol, also highly dispersed oxide nanoparticles were accessible. PtCo catalysts obtained via this pathway were very active for the hydrogenolysis/hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran[12], materials with smaller PtCo nanoparticles with sizes around 1.5 nm were highly interesting systems for the hydrogenation of the phenolic groups in bio-oils[22], and Co_3O_4 nanoparticles synthesized on such polymers (Fig. 2) were very active and selective (S typically exceeding 95 %) in the selective transfer hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols[42].

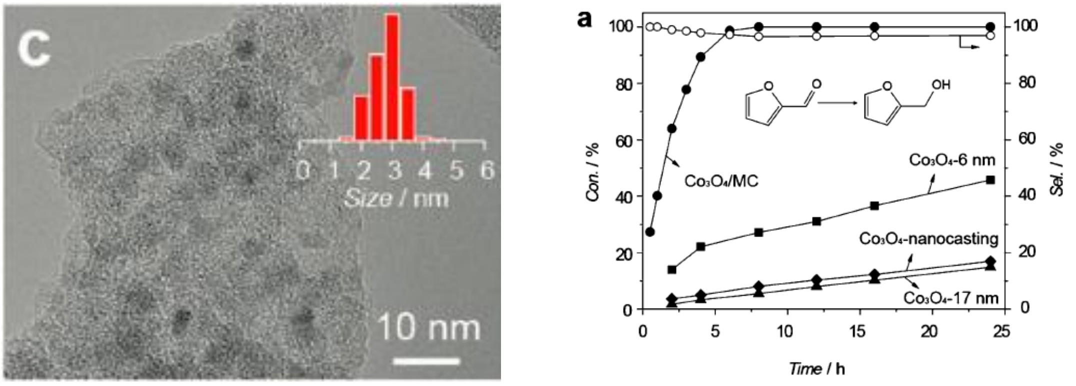


Fig. 2: Co_3O_4 nanoparticles on carbon obtained via an aminophenol-formaldehyde resin with particle size distribution as inset (left). Conversion (filled symbols) and selectivity (open symbols) in the transfer hydrogenation of furfural with isopropanol over different catalysts (right).

Future directions: The development in the field of nanoengineering of solid catalysts has been rapid and is expected to continue this way also in the next years. The work in this field will thus remain at approximately the same level, and for both classes of catalysts described in more detail in this section, possible commercialization will be explored. Thus, in addition to studies broadening the range of materials and reactions, concepts for upscaling will become more important.

Publications resulting from this research area: 1, 3, 4, 6, 14, 17, 20, 30, 34, 36-38, 41, 42, 45, 46, 50, 53, 56

External Funding: BMWI, CoE TMFB

Cooperations: C. Lehmann, W. Schmidt, H. Tüysüz, C. Weidenthaler (Mülheim); K. Mayrhofer (Düsseldorf, DE); V. Peinecke (Duisburg, DE); O. Terasaki (Stockholm, SE); R. Schlögl (Berlin, DE); H. Wiggers (Duisburg, DE)

2.3.3 Research area "Novel Catalytic Concepts"

(F. Schüth)

Involved: M. Bilke, R. Eckert, A. Grünert, S. Immohr, W. Kersten, H. Schreyer, M. Soorholtz, M. Thomas, T. Trotus, D. Wendt, T. Zimmermann

Objective: This research area is composed of projects of a highly exploratory, but at the same time very exciting nature, where typically only one or two students or post-docs work on a given topic. Unusual reactions or unusual approaches are studied in this research area in an exploratory approach in order to assess, whether more intensive efforts are justified in the future. Topics covered in the research area include catalytic methane activation in oleum, acetylene conversion, mechanocatalytic reactions, and the synthesis of oligomethyleneethers.

Results: The study of mechanocatalytic reactions originates in the work on complex hydrides, was then extended to mechanocatalytic depolymerization of biomass, and finally to mechanocatalyzed gas-phase reactions. The mechanocatalytic depolymerization of biomass is by now well established and also used by several other groups world-wide. The focus of the current work in this field is the understanding of the mechanocatalytic reaction. Here a cooperation with the group of Harald Fuchs (Münster), who is an expert in in-situ scanning probe microscopies has been initiated. The current hypothesis concerning the mechanism of the mechanocatalytic depolymerization of cellulose is the concerted action of a proton and mechanical force, leading to a favorable deformation of the molecule. This is being simulated on a surface by depositing cellobiose, coadsorbing an acid, and then pressing on the molecule with the tip of an atomic force microscope to induce the reaction. This is a very high risk project, but first, preliminary results suggest that p-toluenesulfonic acid around cellobiose on a surface form specific structures (Fig. 1).

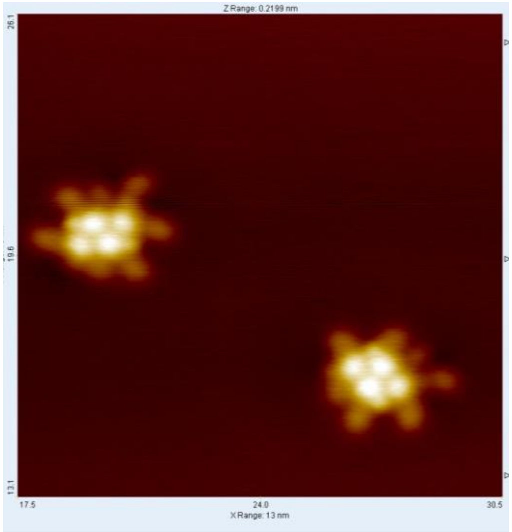


Fig. 1: STM images of cellobiose coadsorbed with p-TSA on Ag(111). Structures typical for certain deposition conditions and possibly cellobiose surrounded by p-TSA molecules (ccoperation H. Fuchs).

For the mechanocatalytic gas-phase reactions, rate increase by three orders of magnitude had been reported for CO-oxidation during in situ milling in a planetary ball mill. These studies have been extended to the preferential oxidation of CO in hydrogen [22]. Surprisingly, for this reaction the selectivity and activity increased with decreasing temperature, and at -40°C 81 % CO conversion at 95 % selectivity were achieved for the standard conditions for this reaction, which is attributed to slower healing of high activity defects at low temperature. For this reaction, the rate increase by ball milling amounts to approximately four orders of magnitude.

The catalytic chemistry of acetylene has been rather neglected over the past decades, in spite of many advances in catalysis in general[18]. Since acetylene could become an interesting feedstock in the future again, a program exploring acetylene chemistry has been initiated. A fully remote controlled, automated flow system has been constructed which allows safe handling of acetylene up to pressures of 30 bar, allowing both batch and continuous reactions. The work is of a highly exploratory nature, and several different reaction pathways starting from acetylene have been explored. The attempts were successful in acetylene-ethylene cross-metathesis to result in butadiene over known metathesis catalysts, which was the first reaction of this kind[35]. However activities are too low for practical applications. Solid catalysts suffer from very rapid deactivation in acetylene streams, which is mostly due to oligomer or carbon formation. However, one class of catalysts, copper on zeolites, and especially copper on zeolite Y, is a highly interesting system for the dimerization of acetylene to result in a high yield of C_4-products. Considering the possible shortage of these fractions due to the lighter feeds used in steam crackers, this could become an interesting development line also for industrial implementation.

Methane activation with a solid version of the Periana-catalyst had already been described in previous reports. Intensive efforts, involving several cooperation partners, have revealed a comprehensive picture of the structure of the solid: it is indeed to a large fraction a solid analogue of the molecular catalyst[54]. While this is highly interesting, the work on related solids,

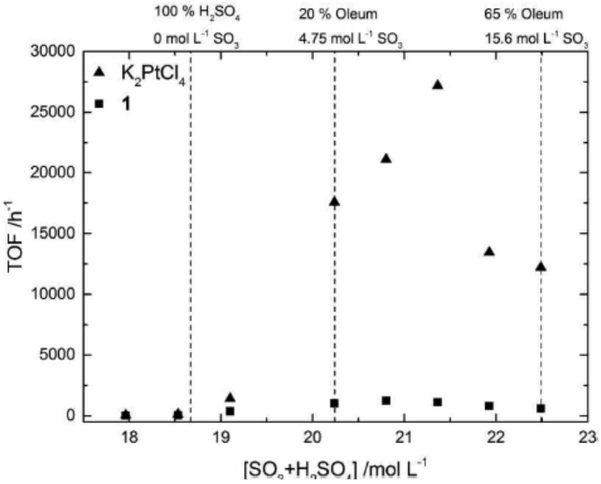


Fig. 2: TOF for methane oxidation in dependence of oleum concentration over K_2PtCl_4 (triangles) and the Periana catalyst $Pt(bpym)Cl_2$ (squares).

in which leaching of active species was observed, led to a spectacular result: It was found that under the right conditions (low concentration of the catalyst, high concentration of SO_3 in the oleum) the catalyst is more than three orders of magnitude more active than reported in the literature, at turnover frequencies close to 30.000 h^{-1} (Fig. 2)[43]. This brings the activity of this catalyst into the same domain as those realized in big commercial processes, such as the Cativa-process or hydroformylation. Also productivities (0.5 kg methanol per liter and hour) are in a range where commercial processes operate. This does, however, not mean that commercial implementation is imminent: the separation of the methylbisulfate from the reaction medium is difficult and costly, and current efforts are directed towards the solution of this problem.

A final project in this research area is directed at the synthesis of oligomethyleneethers (OMEs). These compounds are ideal Diesel-fuel additives, and due to their combustion properties and their higher boiling point superior to dimethylether. Direct synthesis processes from syngas are thermodynamically unfavorable, so that the reaction between methanol and formaldehyde or related compounds is the method of choice. However, this reaction is currently only carried out under batch conditions, which is not optimal. Efforts are therefore directed at the direct synthesis in the gas phase using water-free formaldehyde over different catalysts. This project, however, is still in an early phase.

Future directions: The very nature of the projects in this research area makes it difficult to exactly predict their course. For the mechanocatalytic reactions, the atomic probe microscopy studies to elucidate the fundamental principles of these reactions appears promising, but the interpretation is a substantial challenge which probably also requires support from theory. The formation of C_4 compounds from acetylene is still in an early phase and thus needs to be further studied, moreover, reactions of supported ionic liquid catalysts appear to be promising. Methane activation requires progress in product separation, which will be attempted by formation of compounds which are easier to separate. Finally, the work on OME synthesis is at its beginning, so that initially exploration of catalysts and reaction conditions is on the agenda.

Publications resulting from this research area: 18, 35, 43, 52, 54

External Funding: Industry

Cooperations: M. Antonietti (Golm, DE); B.F. Chmelka (Santa Barbara, US); J. Maier (Stuttgart, DE); H. Fuchs (Münster, DE)

2.3.4 Research area "Biomass Conversion"

(F. Schüth)

Involved: G. Al Shaal, Z. Cao, M. Dierks, J. Engelhardt, J. Hilgert, M. Käldström, M. D. Kaufmann-Rechulski, N. Meine, V. Nese, A. Padovani, C. Pupovac, F. Richter, U. B. Richter, M. Ruby, L. Sahraoui, M. P. Tong, G. H. Wang

Objective: In the last report, biomass conversion was covered exclusively in the report of Roberto Rinaldi, although some of the research was a joint effort between the Schüth and the Rinaldi group. Some of the activities, especially those on lignin valorization, but also partly research on the conversion of other biomass components, moved with Roberto Rinaldi to Imperial College, but some of the activities are also being continued in the department at the Institute, and these activities will be covered here. The objective of this research is the valorization of biomass components, leveraging the catalysts and the concepts developed in the department in other research areas. Especially the possibilities of nanostructured catalysts shall be exploited, but here it is crucial to transfer the elaborate methods for nanostructuring to catalytic materials which are accessible at larger scale and at low cost, since the bulk type conversions and the prices associated with most routes are not compatible with expensive catalysts.

Results: The work on mechanocatalytic depolymerization of lignocellulose, which had been discovered in the previous reporting period, was continued with a focus on the processing and the scale-up of the procedure[16, 32]. The previous studies were all performed in laboratory planetary ball mills, where the energy required for mill operation exceeded the energy content of the products by a factor of approximately 50. In two different Simoloyer ball mills, the energy consumption was reduced to approximately 5 times the energy content of the products for the 100 g scale, and at the kg-scale, the milling energy and the energy content of the products was at the same level. This trend is promising with respect to a possible commercial application of the process.

Along the sugar route, the conversion of glucose to 5-hydroxymethylfurfural (HMF) and then further to 2,5-dimethylfuran (DMF) or other value-added products, such as 2,5-furandicarboxylic acid were and still are in the center of the attention[22]. Although the publication only appeared in this reporting period, in the last report the carbon-supported PtCo catalysts for the almost quantitative conversion of HMF to DMF had already been described. On paper, this would allow an overall yield of more than 75 %

of a fuel molecule (DMF) from cellulose. However, the three steps of the reaction – mechanocatalytic depolymerization of cellulose, conversion of celloligomers to HMF and hydrogenation of HMF to DMF – proceed at different conditions in different solvents. Work was thus directed to adjust the conditions of the different reactions to each other. A highly interesting development in this connection is the conversion of fructose to HMF in a reaction which is not acid/base catalyzed[48]. Based on reports in which ionic liquids had been described as suitable catalysts, with the anion being the active species, such systems were heterogenized in form of a polymer. In alcoholic solution, compatible with the hydrogenation of HMF, fructose could be converted to HMF at more than 70 % yield. More importantly, the majority of the original products are acetals from the reaction of the product with the solvent alcohol, which can be recovered. These studies are being continued in order to develop a coherent and simple process from cellulose to DMF. Parallel to these efforts, also the direct synthesis of other valuable products from HMF is explored. Particularly successful were attempts to synthesize furandicarboxylic acid. With ruthenium supported on modified porous silica, full conversion and 97% selectivity to FDCA can be achieved under optimized conditions[22].

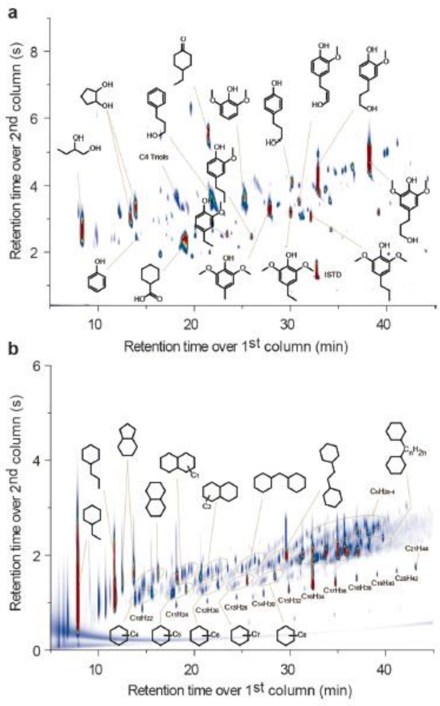


Fig. 1: GC x GC traces of non-pyrolytic bio-oil (top) and the same oil after HDO over PtCo on ordered mesoporous carbon (bottom). After HDO, only aliphatic compounds without oxygen are detected.

Alternative to the depolymerization/sugar conversion-route, the group is also active in the upgrading of bio-oil in the framework of an EU-sponsored project. Bio-oil is a very complex mixture of many highly oxygenated compounds. In order to stabilize it and allow further processing, deoxygenation is crucial. In the framework of the project, the department has the task to develop nanostructured, cheap catalysts for catalytic pyrolysis and for hydrodeoxygenation (HDO) of the bio-oils. For catalytic pyrolysis, hydrothermally synthesized high surface area manganese oxides are amongst the most promising catalysts, resulting in substantial deoxygenation already in the pyrolysis step. These catalysts have been selected for pilot plant pyrolysis experiments which will take place at CPERI/CERTH at Thessaloniki, Greece.

In the HDO, PtCo alloys supported on ordered mesoporous carbons are great catalysts, resulting in deep hydrogenation, so that complete deoxygenation and the production of fully aliphatic hydrocarbon mixtures is possible (Fig. 1)[41]. However, for bio-oil conversion reactions, PtCo catalysts are too expensive, and thus alternatives were explored. Based on the early notion of M. Boudart, that carbides, nitrides, or phosphides of the middle transition metals resemble noble metal catalysts in several of their properties, several such compounds, synthesized by different pathways, were explored as catalysts for these reactions. Nickel phosphide and molybdenum carbide based systems were identified as the most promising systems. With the different catalysts, the selectivity to different product ranges can be controlled: nickel phosphide catalysts result in predominantly aliphatic compounds, while molybdenum carbide favors the formation of aromatic compounds (at even somewhat higher temperatures). Both systems were considered as sufficiently interesting to scale-up the synthesis for pilot plant experiments.

Future directions: Work on biomass conversion will somewhat decrease in importance over the next years. This is partly due to the move of Roberto Rinaldi to Imperial College, partly also due to the completion of the ERC project, in which polymeric catalysts were investigated for biomass conversion. However, studies of conversion reactions via both the sugar route and the bio-oil route will be continued, because biomass conversion is an interesting application field for the nanostructured catalysts which are developed in any case.

Publications resulting from this research area: 2, 5, 7, 12, 13, 15, 16, 32, 41, 47, 48

External Funding: ERC, EU Cascatbel, CoE TMFB

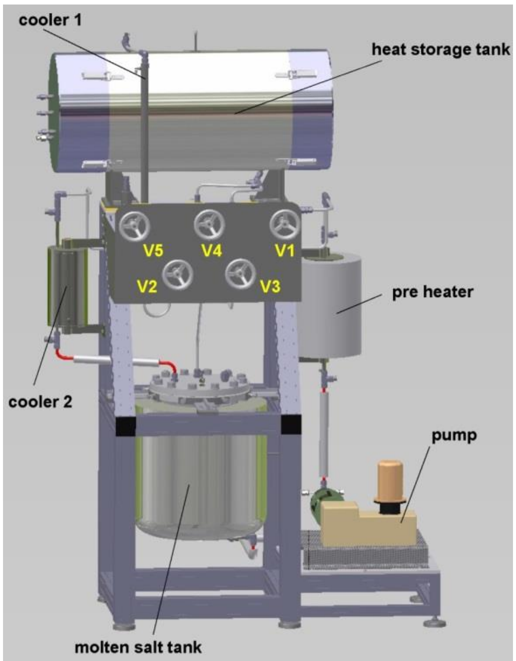
Cooperations: R. Rinaldi (Mülheim, London, UK); C. Fares, W. Schmidt, W. Thiel,
C. Weidenthaler (Mülheim); R. Palkovits (Aachen, DE); D. Serrano (Madrid, ES);
A. Lappas (Thessaloniki, GR); O. Terasaki (Stockholm, SE)

2.3.5 Research Area “Hydrides for Hydrogen and Energy Storage” (M. Felderhoff)

Involved: R. Albert, Z. Cao, A. Dwivedi, O. Kirschmann, D. Krech, M. Ley,
K. Peinecke, M. Meggouh, R. Moury, P. Unkel, C. Weidenthaler, B. Zibrowius

Objective: Aluminium and magnesium based hydrides were intensively studied, both for their structural properties and as potential hydrogen and heat storage materials. Although they are presently not practical for mobile systems, they can be used for stationary fuel cell applications. The activities with these compounds have been focused in order to demonstrate the practicability of these materials for heat and hydrogen storage with fuel cell systems and to explore and characterize new compounds of aluminium based hydrides as possible hydrogen storage materials.

Results: Power-to-heat is one important component future energy systems, but efficient heat storage systems are missing. In the past MgH_2 and Mg_2FeH_6 were extensively characterized at lab scale size as heat storage materials. According to the following equation the material Mg_2FeH_6 can reversibly store heat combined with the uptake and release of hydrogen[70, 71].



Demonstration unit for thermochemical heat storage
Mg_2FeH_6, $T_{max} = 550°C$, molten salt for heat transfer

$Mg2FeH6 + Q \rightleftharpoons 2 Mg + Fe + 3 H_2$ Mg_2FeH_6 shows exceptional stability over thousands of heat storage and heat relase cycles. The worldwide first demonstration unit with Mg_2FeH_6 as heat storage material for temperatures up to 550 °C (5 kg Mg_2FeH_6) was built up. In order to reach these high temperatures we used molten salts as heat transfer medium, because thermo oils are not stable under these conditions. After first successful operation of the system, technical optimization and long term experiments are in progress.

Aminoalane (NH_3-AlH_3) and substituted compounds are possible, but not examined materials for hydrogen. A broad screening of these materials was started in order to understand the chemical behavior and to characterize these materials structurally and physically. For dimethylaminoalane $(NMe_2\text{-}AlH_2)_3$ a plastic crystalline phase has been discovered at T > 332 K. Interestingly, this plastic crystalline phase can be described as an A15 phase, which is normally observed only for micellar systems and for several intermetallic compounds. To the best of our knowledge this study was the first one that reported on an A15 phase for a simple metal organic compound. This plastic crystalline state of $(NMe_2\text{-}AlH_2)_3$ seems to be interesting as ion conductive material for battery applications [66, 69].

While $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ were extensively studied for hydrogen storage applications over the last 15 years, only little information is available about the homologues $RbAlH_4$ and $CsAlH_4$. For both compounds a new direct synthesis method, starting from Rb or Cs and Al-metal under H_2-pressure was developed. A new tetragonal phase of $CsAlH_4$ was discovered and the phase transition from the tetragonal to orthorhombic phase and vice versa was in situ observed with X-ray diffraction. The temperature and the kinetics of this phase transition can be influenced through the addition of $TiCl_3$, which is often used as a catalyst for the decomposition and hydrogenation of complex aluminium hydrides. Nevertheless this effect is not completely understood and more investigations are in progress [57, 61].

Future directions: The size of demonstration projects for heat storage with Mg-based compounds in the temperature range of 400 °C (several hundred kg of heat storage material) will be increased. Use of complex hydrides for heat and hydrogen storage in combination with HT-PEM fuel cell systems for the optimization of the fuel cell performance will be demonstrated, and the properties of unstable hydrides (animoalanes, metal hydrides) in combination with high pressure hydrogen gas systems will be explored, in order to develop new solutions for hydrogen storage for fuel cell automotive systems.

Publications resulting from this research area: 57-72.

External funding: IMPRS SurMat, BMBF, AiF, Energieforschung NRW, CSC China (stipend to C. Zhijie), DAAD (stipend to A. Dwivedi), CDZ (travel stipend to M. Felderhoff)

Cooperations: F. Mertens (Freiberg, DE); D. Bathen, S. Peil (Duisburg, DE), M. Fichtner, A. Leon (Karlsruhe, DE), M. Zhu, L. Ouyang (Guangzhou, CN)

2.3.6 Research Area "Nanostructures and Optical Materials"
(F. Marlow)

Involved: S. Abdellativ, J. Akilavasan, A. Hullermann, G. Mane, L. Messmer, M. Muldarisnur, D. Naumann, M. Rehosek, P. Sharifi, Y. Xiong

Objective: Novel functional materials consist of a hierarchy of building blocks which have to be assembled by precise and tunable methods. In this research area we investigate fundamental aspects of processing steps and nanostructure building block formation, and the tuning of optical and photocatalytic properties of materials, and their system integration.

Results:

Opals. Photonic crystals (PhCs) are highly ordered nanostructures with at least one length scales in the order of the wavelength of light. They have specific effects on electromagnetic fields. The self-assembly of these materials especially of artificial opals was investigated in our group. The improvement and understanding of one of the best-defined opal fabrication methods (capillary deposition method) was the focus of the research. Opal films fabricated by this method can be understood as intergrowth structures of two different fcc lattices, each of them interrupted by stacking faults. We found out that the fcc-fcc twinning leads to relatively big domains which are not limiting to potential applications. The mean free path for photon can reach about 100 µm which is the largest value published in literature.

The detailed understanding of the opal self-assembly process was the main focus of our research during the last years. The opal formation can be divided into two temporal phases: the wet assembly and the drying. Both are of relevance for the quality of the opals. We have followed these two temporal phases by optical spectroscopy in-situ. In the second phase, a counter-intuitive surprising process (“v-event”) was discovered. In addition, the significant rearrangement processes during and after water extinction have been

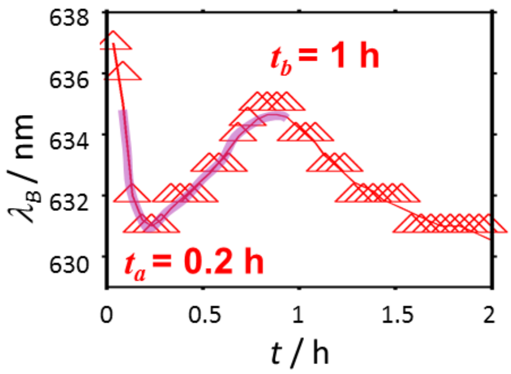


Fig. 1: The v-event in opal formation. The Bragg-peak position shifts during the drying process mainly due to shrinking. The general red shift is interrupted for a short period after about 15 min due to nanostructure dewetting. From: Marlow et al. *Angew. Chem.* **2014**.

studied in detail. Optical microscopy, electron microscopy, optical spectroscopy, and neutron scattering have been used for opal film characterization.

DSSC mechanisms and modeling. Dye-sensitized solar cells (DSSCs) are a promising type of alternative solar cells. After 20 years of continuous research, but slow progress with these cells, the interest has increased in the last years again. Therefore, we have developed techniques for the reliable fabrication, characterization, and description of these solar cells. Besides the use of modified semiconductor electrodes, an improved understanding of the charge transport mechanisms in these solar cells turned out to be crucial. Our measurements have shown clear inconsistencies for the current standard model of the DSSC mechanism. The development of a new basic understanding is the current project in this field.

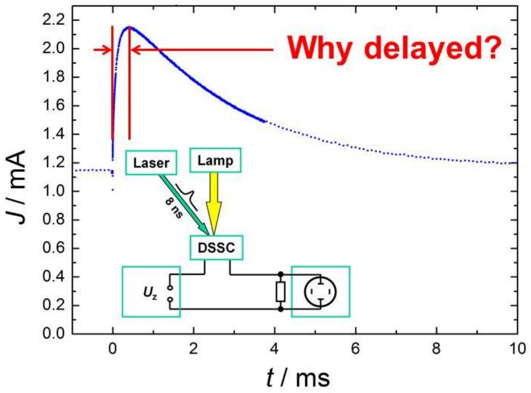


Fig. 2: One of the unsolved problems in DSSC research. Transients after short pulse laser excitation show a delay which is not explained by the current standard model. From: Marlow et al. *Adv. Mater*. **2015**.

Furthermore, we work on numerical DSSC modeling based on trustworthy input data. Especially, the applied porous semiconductor has unknown scattering properties and refractive indices. Recently, we succeeded in their determination. Besides the optimization of the cells, this enables a better interpretation of optical spectroscopy data obtained for DSSCs.

New photocatalytic reaction systems. DSSCs are quite complex, but highly efficient photoelectrochemical systems. They can give a number of inspirations for more efficient photocatalytic reaction systems as well. Most, if not all heterogeneous photocatalytic systems currently studied suffer under inefficient use of visible photons, strong electron-hole recombination, and unfavorable mutual influence of electron and hole reactions. Therefore, we developed a new concept applying sensitized semiconductors at liquid-liquid interfaces. This could solve the three mentioned photocatalytic problems: sensitizer molecules can enhance the visible light absorption, electron-hole recombination can be suppressed by band bending techniques, and the two different photochemical reactions are located in two different media. The realization of this concept requires many partial steps. Currently, we develop an appropriate measurement setup and study the transport of charges through liquid-liquid interfaces.

Janus-Particles. For efficient catalytic and photocatalytic processes at interfaces as e.g. described above, one needs stable incorporation of solid particles into these interfaces. Janus particles are known since long to have interesting and stable incorporation behavior. However, their synthesis is up to now fragile, not well tunable, and not well up-scalable. Therefore, we have studied two synthesis pathways in detail and extended them for our purpose. The Feyen pathway developed by Schüth et al. was extended to a photo-catalytically interesting system by site-selective TiO_2 coating. The wax-masking pathway (Granick et al.) was successfully up-scaled and is now our most promising basis for further interface incorporation investigations.

Future directions: The activities in the DSSC field will be continued. The understanding of the working mechanism of DSSCs is regarded as a crucial issue which is not satisfactory in the literature up to now. We will work on a modified mechanistic DSSC model. Novel DSSC-inspired photocatalysts will be another long-term topic of our research.

Publications resulting from this research area: 73-77

External funding: IMPRS SurMat, Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft.

Cooperations: A. Khalil (Cairo, EG), C. Chan (Tempe, US), N. Benson (Duisburg, DE), H. Wiggers (Duisburg, DE), H. Tüysüz (Mülheim/Ruhr, DE), P. Schulze (Mülheim/Ruhr, DE)

2.3.7 Research Area "Novel Processes and Catalysts for Selective *syngas* Conversion"

(G. Prieto)

Involved: N. Duyckaerts, J. Kim, T. Haak, A. Rocha-Vogel.

Objective: Valorization of delocalized, petroleum-alternative feedstocks, such as associated- and shale-gas gas or lignocellulosic biomass, into liquid fuels and platform chemicals, e.g. via *syngas* (H_2+CO+(CO_2)), is hampered by their envisaged small scale and corresponding economy-of-scale penalties. Process intensification is thus an enabling prerequisite for such approaches. In particular, the integration of two catalytic functions in a single reactor, to effect sequential reactions in tandem, gains increasing interest as intensification strategy. The overriding goal of this research area is to gain fundamental insight into, and purpose-design innovative solids catalysts for, tandem catalytic processes for selective *syngas* conversion.

Results: The research has focused initially on the single-step conversion of *syngas* into liquid hydrocarbons via the one-pot integration of the Fischer-Tropsch (FT) and hydrocracking reactions. Our investigations on the processing of model FT hydrocarbon feedstocks on a Pt/H-ZSM-5 bifunctional hydrocracking catalyst revealed the impact of the gas atmosphere on the reaction pathway for paraffin and α-olefin primary FT products [52]. Unlike under standard hydrocracking conditions (H_2 atmosphere), the presence of *syngas*, which mimics the conditions encountered in the tandem process, results in severe poisoning of the platinum (de)hydrogenation functionality by strong CO adsorption, which causes a notable divergence in the reaction pathway for each type of FT product. Under these conditions, particularly α-olefin primary FT products are notably more reactive, as they by-pass the dehydrogenative activation step required for paraffins, contribute to moderate the undesired secondary cracking, likely via an enhanced competitive adsorption on the acid sites, and undergo oligomerization reactions, bringing about an extra, acid-catalyzed chain-growth mechanism which adds to restricting the overall yield to undesired light (C_{4-}) hydrocarbon products. Our results highlight the significance of the nature of the FT primary products exchanged by the tandem catalysts for the overall efficiency, thus pointing to it as a major design variable.

Under relevant reaction conditions, pore mass transport phenomena can notably affect, and therefore serve as lever on, the primary FT product pattern. In this respect, we have developed a research platform to design FT supported cobalt-based catalysts with bespoke multimodal porosities. Our synthesis efforts rely on the combination of soft- and hard-templating routes with structural diagnostics obtained, a.o., by tomographic FIB-SEM imaging (Figure 1a). On the other hand, catalytic experiments have revealed a striking impact of porosity on the primary FT product pattern. As a showcase, Co/Al_2O_3 catalysts featuring a trimodal macro-macro-mesoporous topology lead to up to an order of magnitude higher olefinicity of the FT products compared to conventional mesoporous counterparts, due to the notably shorter effective (mesopore) transport distances for most primary α-olefin products, which limits their secondary processing into paraffin products via chain-reinsertion and hydrogenation reactions on the cobalt sites. These results are currently being valorized to optimize the overall efficiency of a tandem process for the single-step production of wax-free liquid hydrocarbons, by independently engineering the chemical and spatial intimacies between the integrated Fischer-Tropsch and hydrocracking catalysts.

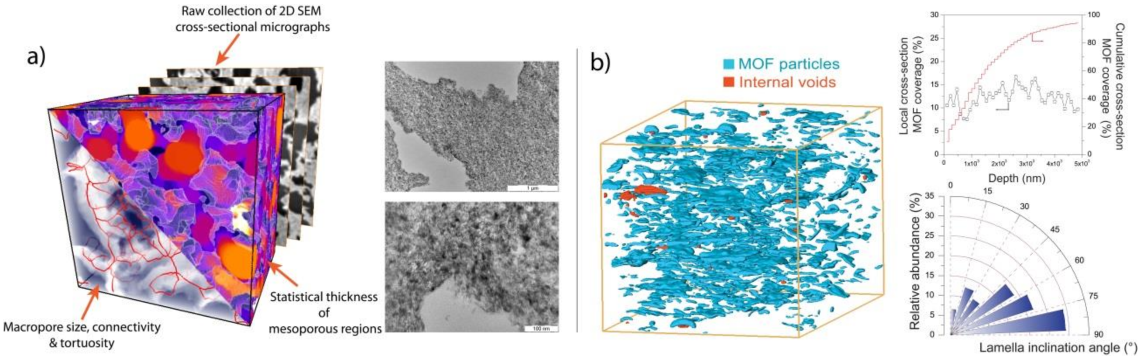


Fig. 1: a) Schematic representation of the 3D macroporosity quantification in multimodally porous Co/Al_2O_3 Fischer-Tropsch catalysts by FIB-SEM tomography (left), and TEM images showing the confinement of cobalt nanoparticles within the mesopores (right); b) Segmented FIB-SEM tomogram (left) and quantification of the permeation cross-section coverage and MOF lamellae orientation (right) for a composite membrane bearing lamellae Cu-BDC MOF nanocrystals within a polyimide matrix[80].

The 3D microstructural quantification platform developed in the framework of this research area has also been leveraged in a spin-off project, in cooperation with researchers at ITQ (CSIC, Spain) and TU Delft (The Netherlands), to assist the fundamental understanding and development of novel MOF(metal-organic-framework)-polymer composites for gas-selective membrane applications (Figure 1b) [80].

Future directions: We aim to extend the implications of our recent findings to develop other catalysts and (tandem) processes for the selective conversion of *syngas* into relevant platform chemicals, such as long-chain olefins and oxygenates.

Publications resulting from this research area: 21, 29, 36, 45, 52, 78-82

External funding: European Research Commission (individual FP7 Marie Curie Actions grant to G. Prieto); Fonds der Chemischen Industrie (funding for consumable costs to G. Prieto).

Cooperations: A. Lorke (Duisburg, Essen, DE); N. Fischer (Cape Town, ZA);
F. Llabrés and A. Corma (Valencia, ES); F. Kapteijn and J. Gascon (Delft, NL)

2.3.8 Research Area “Formation of Nanoporous Silicates”
(W. Schmidt)

Involved: M. Castro, I. Lim, H. Bongard

Objective: Nanoporous silicates are essential components of many solid state catalysts. Their porosity, high internal surface area, and broad range of functionality make them highly valuable in heterogeneous catalysis. Synthesis of nanoporous silicates has seen tremendous progress in the last decades. However, the very basic formation processes on molecular level are often barely understood. Consequently, zeolite nucleation and crystallization are currently subjects of widespread investigation. Unravelling processes involved in the formation of nanoporous silicates is subject of this research area.

Results: In the last three years we focused preferentially on the formation of zeolite beta starting from molecular precursors [44,83]. In collaboration with laboratories in Versailles, Leuven and Lund the entire formation of the zeolite starting from clear solutions and ending in the crystalline zeolite was unrevealed by using complementary analysis methods including small angle X-ray scattering (SAXS), X-ray diffraction (XRD), mass spectrometry (MS), liquid state nuclear magnetic resonance spectroscopy (^{29}Si, ^{27}Al, ^{13}C, ^{1}H, ^{14}N NMR), transmission electron microscopy at cryogenic temperature (cryo-TEM), and scanning electron microscopy (SEM). We conclusively showed that formation of zeolite beta from clear solutions starts by formation of loose aggregates of oligomeric silicate species (Figure 1). These nanoaggregates (or primary nanoparticles) contained not only different oligomeric silicate species but also all aluminum present in the solution as well as tetraethylammonium cations, the structure directing agent that triggers the formation of zeolite beta. The compounds within these aggregates readily exchange with those in the surrounding solution. At higher silicate concentration, the nanoaggregates get transformed into secondary nanoparticles via silicate condensation and motional freedom of the individual compounds gets significantly restricted. At low silicate concentration, silicate condensation and formation of nanoparticles proceed only at elevated temperature. Irrespective of the temperature at which the

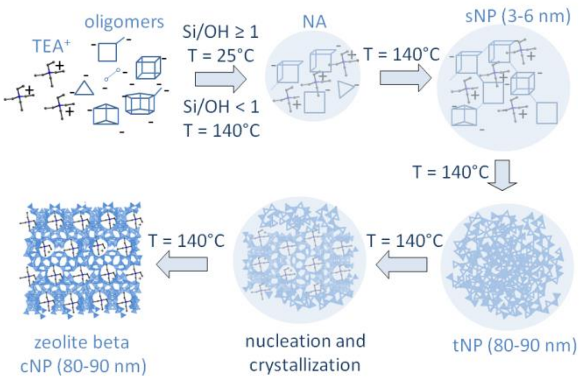


Fig. 1. Formation process of zeolite beta from clear solution [44].

secondary nanoparticles were formed, upon heating they grow to form much larger but still amorphous tertiary nanoparticles. Simultaneously, the degree of silicate condensation increases. Aluminum is present exclusively in four-fold coordination to silicate within the nanoparticles. During heating the formation of zeolite beta proceeds via nucleation within the amorphous nanoparticles, followed by crystal growth from the zeolite nuclei. The resulting zeolite beta crystallites are of the same size as the amorphous tertiary nanoparticles, indicating a successive transformation of the amorphous particles into the crystalline materials. Particle growth as expected from Ostwald ripening is thus observed only for the amorphous silicate nanoparticles but not for the crystalline zeolite.

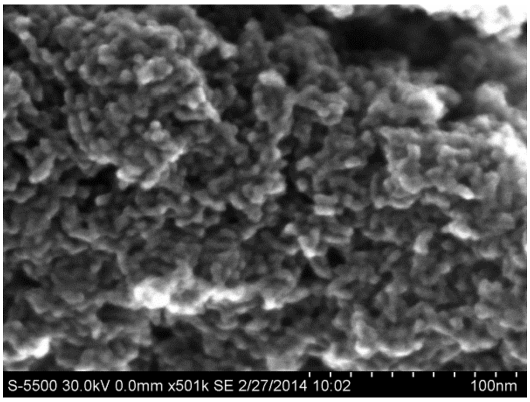


Fig. 2. SEM image of zeolite beta nanorods obtained with amphiphilic structure-directing agent.

Using alternative structure directing agents with long hydrophobic alkane chains, we could show that the basic formation processes are quite similar to those described above. However, due to the amphiphilic nature of these structure directing agents, cylindrical primary and secondary nanoparticles with core-shell structure are formed. Nucleation and crystallization proceed then from these cylindrical silicate nanoparticles whereby the hydrophobic side chains of the structure directing agents prohibit the formation of larger zeolite particles. The resulting materials consequently consist of zeolite beta nanorods (Figure 2) with diameters of about 4 nm and lengths of about 10 nm. The zeolite nanorods are aggregated to form materials with hierarchical micro- and mesopores, the mesopores being the voids between the aggregated rods.

Future directions: The studies on zeolite formation will be extended to other systems to expand the understanding of zeolite formation and modified zeolites will be used as the basis of bi-functional catalysts for the catalytic conversion of poisonous gas compounds.

Publications resulting from this research area: 10, 44, 83, 84

Cooperations: F. Taulelle (Versailles, FR); C. Kirschhock (Leuven, BE), V. Alfredsson (Lund, SE), F. Schüth (Mülheim/Ruhr, DE)

2.3.9 Research Area "Carbon-supported Transition Metal Oxide Catalysts" (W. Schmidt)

Involved: C. Weidenthaler, A. Pommerin, J.C. Tseng, H. Bongard, S. Puthenkalam, D. Gu, G. Wang

Objective: Nanoscopic transition metal oxides have been shown to be efficient catalysts for the conversion of gaseous compounds, such as CO, from gas steams even at room temperature. The investigation of supported transition metal based materials for removal of poisonous compounds from gas streams and chemical conversion is subject of this research area.

Results: A number of transition metal oxides has been deposited within the nanopores of activated carbons [85,88]. The restricted space in the nanopores of the carbons allowed only for formation of nanoscopic oxide particles. As for an example, the materials obtained by deposition of CuO/ZnO or hopcalite-like within activated carbon were efficient in removal of NO_2 and NH_3 from air streams at room temperature [87,89,90]. The efficiency of the active adsorbers were significantly better than those of the pure carbon materials. XRD analyses of the oxide particles within the activated carbons showed that the nanoscopic CuO is generally present as a crystalline phase whereas ZnO is present preferentially as amorphous oxide or hydroxide at lower oxide loading.

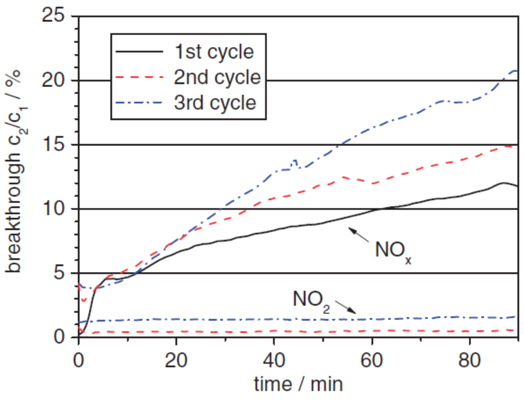


Fig. 1a. Breakthrough of NO_2 and NO_x through activated carbon impregnated with CuO/ZnO. (23 °C, 50% RH, $c_1(NO_2)$ = 4 ppmV, $c_1(NO)$ = 0 ppmV) [90..

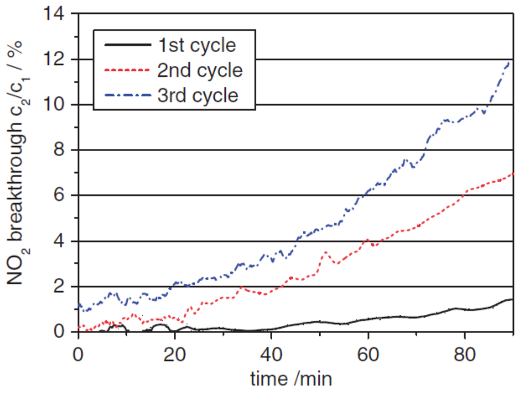


Fig. 1b. Breakthrough of NO_2 through pristine activated carbon. (23 °C, 50% RH, $c_1(NO_2)$ = 4 ppmV, $c_1(NO)$ = 0 ppmV) [90.]

At higher loading a fraction of ZnO is also observed as crystalline phase. Line profile analyses of XRD data show that the average particle sizes of the oxidic phases lie in the range of 2.5 – 3.5 nm [89]. EDX mapping proves that the oxides are dispersed homogenously over the entire activated carbon particles. The activated carbons with different loadings of mixed oxides are active in reducing the concentration of NO_2 if used in thin layer adsorbers as used in car cabin air filters. As shown in Figure 1a, NO_2 breakthrough is greatly reduced in carbons impregnated with CuO/ZnO if compared with the pristine activated carbon (Figure 1b) and long term activity of the adsorber material is significantly enhanced if impregnated with the mixed oxides.

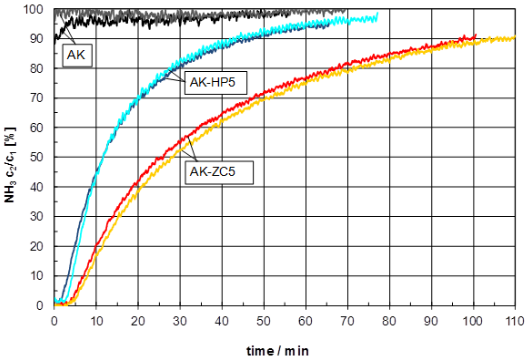


Fig. 2. Breakthrough of NH_3 through activated carbon impregnated with 5 wth% hopcalite or CuO/ZnO. (23°C, 50%RH, c1(NH_3)=4ppmV).

Similarly, even though not as efficiently as for NO_2, NH_3 breakthrough through activated carbon loaded with hopcalite or CuO/ZnO is reduced (Figure 2). NH_3 retardation from can be increased to some extent by increasing the oxides loading but oxide contents of more than 30 wt% do not result in significant further increase of NH_3 removal [90].

The oxidic compounds enhance the interaction of the adsorber material with NO_2, NO_x and NH_3, likely due to interaction of the oxide surfaces with the respective molecules. Furthermore, NO_2 gets reduced to NO by reaction with the carbon. This reaction proceeds much faster if the mixed oxides are deposited within the carbon. Catalytic activity of the oxide seems to exist even at room temperature, e.g., via cooperative interaction of the gas molecules with the oxide surfaces and the carbon.

Future directions: The studies on metal oxide loaded activated carbons or on ordered mesoporous carbons have shown the potential of such materials as catalysts. However, the role of the oxidic compounds, catalytic or not, and its cooperative interaction with the carbon surface remains speculative and further research must focus on the understanding of this interaction.

Publications resulting from this research area: 31, 42, 85, 87-90

External funding: Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF, stipend to J. C. Tseng)

Cooperations: U. Sager, F. Schmidt (Duisburg, DE), F. Schüth (Mülheim/Ruhr, DE)

2.3.10 Research Area “Nanostructured Inorganic and Hybrid Materials for Water Splitting” (H. Tüysüz)

Involved: K. Chen, X. Deng, G. Dodekatos, T. Grewe, S. Öztürk, S. Schünemann, M. Yu

Objective: The motivation behind this research area is the development of new methods and the improvement of existing synthetic approaches for the preparation of novel nanostructured inorganic and hybrid materials for solar energy conversion, with a focus on the different aspects (photocatalytic, electrochemical, and photoelectrochemical) of water splitting. The aim is the evaluation of the key physical and chemical properties of nanostructured materials to allow the development of more effective water splitting catalysts.

Results: *Regarding photocatalytic water splitting*, the role of junctions in tantalate based composite materials—where a more effective charge separation is expected—was investigated. By using a hydrothermal method, a series of novel amorphous and crystalline tantalates with various morphologies was prepared. The junctions between amorphous and crystalline tantalates and also junctions between two crystalline phases, namely perovskite and pyrochlore, were found to improve the efficiency of the photocatalysts significantly [95, 98]. In order to investigate the influence of the junctions in a more well-defined system, a new process based on soft templating was developed. By using this modified approach, a series of amorphous ordered mesoporous tantalates with similar textural parameters and different sodium to tantalum ratios was prepared. The effect of the junctions and improved hydrogen production rate could also be observed for this series of materials, if sodium was incorporated into the composite structure [113]. Besides the modified hydrothermal and templating methods, a new approach was developed for *in-situ* photocatalyst preparation. The process—which is called direct injection— utilizes a metal alkoxide as starting precursor that undergoes hydrolysis, condensation and poly-condensation in a methanol-water mixture under light illumination. This results in nanostructured amorphous materials that show even higher hydrogen production rates than crystalline materials [100].

Regarding electrochemical water splitting, we use ordered mesoporous structures as model system to evaluate the effects of key physical and chemical properties on the performance of materials to gain new insight on the oxygen evolution reaction (OER) and develop more effective non-noble metal based electrocatalysts. By doing so, the effects of the morphology, symmetry, dimension, doping, and composition of the materials on the activity of the OER catalysts could precisely be demonstrated [86, 92, 96]. Furthermore, it was discovered that there is a strong synergy between cobalt and nickel that results in one of the most active transition metal oxide based electrocatalysts for water splitting. After a simple electrochemical activation, which was attributed to incorporation of iron species from the electrolyte, the performance of nickel cobalt oxide could be significantly enhanced. Furthermore, an effective pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) catalyst for electrochemical hydrogen evolution under acidic conditions was discovered. The developed catalyst is as effective as platinum and has the potential to replace this noble metal for electrochemical hydrogen production [109].

In addition, some novel templates were implemented that allow the preparation of hierarchical nanostructured metal oxides. Spent tea-leaves were used as hard templates to prepare nanostructured Co_3O_4 and also mixed oxides. The outcome of this cheap and scalable templating approach is uniform, high surface area nanocrystals with remarkable activity for OER [104]. A hierarchical Co_3O_4 structure that consists of a solid mesostructured skeleton decorated with small Co_3O_4 was prepared via hard templating, using mesoporous silica spheres as a dual template. The pores and the voids between the mesoporous silica spheres can be simultaneously templated, which yields a multifunctional hierarchical structure. This material shows good performance for photo- and electrochemical water splitting [112].

Regarding photoelectrochemical water splitting, we have been focusing on the synthesis of hybrid organometal halide perovskite (OHP, see right SEM image) and $BiVO_4$ in well-defined inverse opal morphology to construct a tandem cell for hydrogen production. For this purpose, an innovative process, based on a colloidal crystal templating approach, was developed to prepare organometal halide perovskites in an inverse opal morphology [99]. Through solvent engineering and the choice of the polystyrene spheres as hard template, a range of different OHP in inverse opal morphology was fabricated. Furthermore, a systematic post-treatment process was established where the halide ions in the perovskite structure could be exchanged in the gas phase to tune the crystal structure and the band gap of perovskite semiconductors with retention of morphology [111]. In addition, OHP and

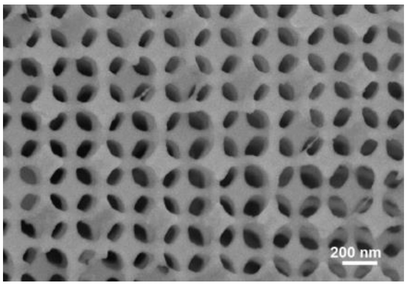


Fig. 1. SEM image of OHP inverse opal

$BiVO_4$ inverse opals were also prepared as thin films on conductive substrates through the same approach by using an assembly of polystyrene spheres as a hard template [108].

Future directions: Future research will include investigations to achieve a better understanding of the activity of amorphous materials for solar water splitting; this includes the design of binary and ternary non-noble metal oxides for electrochemical water splitting and *in-situ* Raman spectroscopy studies on electrocatalysts, in order to monitor surface changes in the materials and determine the possible active species. For the photochemical water splitting, the goal will be to improve the stability of the OHP and the construction of a tandem cell for solar hydrogen production. Moreover, nanostructured carbon based materials will be designed for electrochemical water splitting, and work on the oxidation of glycerol will be developed as a new direction.

Publications resulting from this research area: 24, 86, 92, 95, 96, 98, 99, 100, 101, 104, 108-114

External funding: Fonds der Chemischen Industrie, DFG Cluster of Excellence RESOLV, MAXNET Energy Consortium, IMPRS RECHARGE, BMBF

Cooperations: F. Schüth, C. Weidenthaler, W. Schmidt (Mülheim, DE), C. Chan (Tempe, US). U. Apfel (Bochum, DE), E .Garnett (Amsterdam, NL)

2.3.11 Research Area “Advanced X-ray Diffraction Techniques”

(C. Weidenthaler)

Involved: T. Bernert, M. Felderhoff, W. Kersten, J. Knossalla, R. Moury, S. Ortatatli, L. Pagliari, O. Petrova, W. Schmidt, V. Tagliazucca, J. Ternieden, J.C. Tseng, H. Tüysüz, A. Woyk

Objective: Major focus of all research activities is on methods for the analysis of structure-properties relations of nanosized functional materials. These include crystal structure solution from powder diffraction data, microstructure analysis and atomic pair distribution function analysis (PDF). Over the last decade the realization of *in situ* analytics, especially using in-house instrumentation, became more important. The coupling of two or more probes opens new insights into functional materials under reaction conditions. New tailor-made sample environments for different applications have been designed and built in cooperation with the workshop of the institute.

Results: As a continuation of detailed crystallographic investigations of complex hydrides as potential hydrogen storage materials (see report 2011-2013), different sample environment cells were developed for *in situ* diffraction studies of dehydrogenation and rehydrogenation reactions of potential hydrogen storage materials using *in-house* powder diffractometers [57, 61, 63, 64]. Usually, such experiments are performed at synchrotron facilities which provide high fluxes. However, the special design of the sample cells and

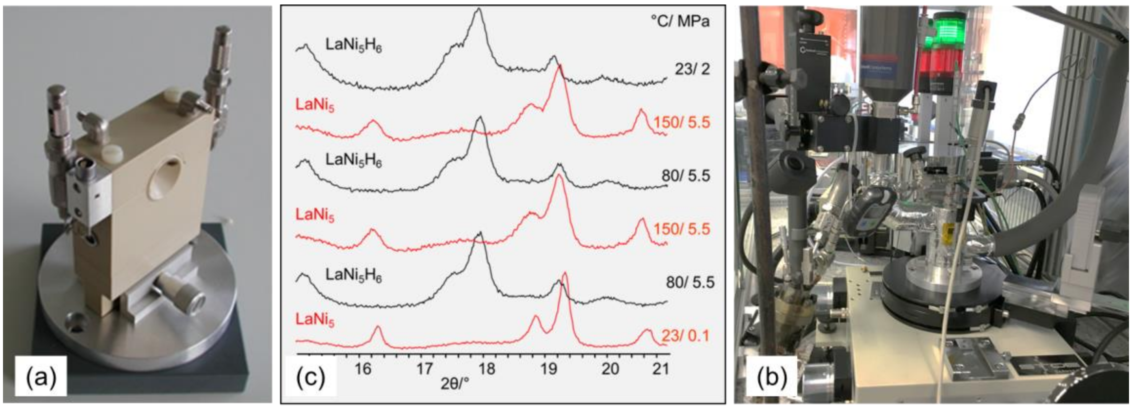


Fig. 1.(a) *in situ* XRD cell made of PEEK, (b) *in situ* diffraction patterns collected during hydrogenation and dehydrogenation of LiNi$_5$ at 5.5 MPa but different temperatures, (c) low temperature-high-pressure cell.

the choice of window materials make the cells suitable for laboratory diffractometers. One type of sample cells shown in Fig.1a covers the temperature range between r.t. and 180 °C and H_2 pressures up to 30 MPa [64]. Phase changes during reversible hydrogenation can be quickly monitored by *in situ* diffraction experiments as illustrated for $LaNi_5$ (Fig.1b) Data quality after 10 min data collection time per scan is sufficient to follow the structure changes qualitatively. Another sample cell which enables diffraction experiments between 173-500 K and H_2 pressures up to 20 MPa (Fig. 1c) is currently under evaluation. This sample environment was designed for the special investigation of unstable aminoalanes as prospective hydrogen carriers in combination with high pressure gas tanks or as catalysts [66, 69].

In situ diffraction can be performed during catalytic reactions even under harsh experimental conditions. Ammonia decomposition is one of the reactions which has not been intensively studied under reaction conditions in the past due to the corrosive properties of ammonia. We have installed a reaction chamber with a computer-controlled gas distribution system which makes studies of catalysts in pure ammonia feasible. Based on the *in situ* studies, we obtained very detailed insights into changes of inorganic catalysts with respect to crystal structures, chemical composition, and microstructure which are not accessible by any *ex situ* experiment [120, 122]. A direct coupling of the reaction chamber on the diffraction instrument with a gas analysis system (GC, MS) for the direct analysis of the reaction gases could also be realized. Unfortunately, parts of the commercial reaction chamber are made of steel which acts as catalyst itself. To overcome this problem, a new catalysis cell was designed which is completely built of inert quartz glass and which can be coupled with gas detection systems (Figure 2). This setup enables the simultaneous collection of diffraction data and catalytic conversion data.

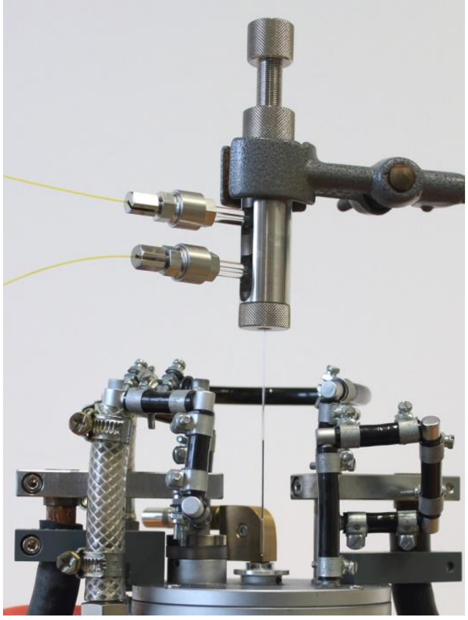


Fig. 2: reaction cell for *in situ* catalysis XRD experiments

Not only crystalline compounds are active catalysts but also disordered or even amorphous materials can be highly active. The local structures of such compounds become accessible if the diffuse scattering contribution to a diffraction pattern is considered by atomic pair distribution function analysis (PDF). Recently, we have performed temperature dependent *in situ* PDF studies of electrocatalysts at a synchrotron radiation source. From the analysis of the data, the formation of alloys from the precursors can be monitored as well as disordering/ordering phenomena taking place during heating and cooling of the catalysts.

Future directions: In addition to the development of *in situ* diffraction methods we will also establish *in situ* techniques to the surface spectroscopy (XPS) of inorganic catalysts. The *in situ* PDF studies will be extended to study the formation and local structures of highly active amorphous photocatalysts such as sodium tantalum oxides or titanium oxide.

Publications resulting from this research area: 57, 61, 63, 64, 66, 69, 120, 122.

External funding: BMBF

Cooperations: F. Schüth, M. Felderhoff, W. Schmidt (MPI Mülheim, DE), B. Hauback (Kjeller, NO), J. C. Jia (Shandong, VC), Michael Römelt (Bochum, DE), Drew Sheppard (Curtin, AU), M. Fischer (Bremen, DE), J. Ruiz-Fuertes (Valencia, ES), F. Mertens (Freiberg, DE)

2.3.11 Publications 2014-2016 from the Department of Heterogeneous Catalysis

Schüth

(1) Asahina, S.; Suga, M.; Takahashi, H.; Jeong, H. Y.; Galeano Nunez, D. C.; Schüth, F.; Terasaki, O. *APL Materials* **2014**, *2*, 113317/1-7.

(2) Käldström, M.; Meine, N.; Farès, C.; Schüth, F.; Rinaldi, R. *Green Chem.* **2014**, *16*, 4994-4994.

(3) Baldizzone, C.; Mezzavilla, S.; Carvalho, H. W. P.; Meier, J. C.; Schuppert, A. K.; Heggen, M.; Galeano, C.; Grunwaldt, J.-D.; Schüth, F.; Mayrhofer, K. J. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 14250-14254.

(4) Suga, M.; Asahina, S.; Sakuda, Y.; Kazumori, H.; Nishiyama, H.; Nokuo, T.; Alfredsson, V.; Kjellman, T.; Stevens, S. M.; Cho, H. S.; Cho, M.; Han, L.; Che, S.; Anderson, M. W.; Schüth, F.; Deng, H.; Yaghi, O. M.; Liu, Z.; Jeong, H. Y.; Stein, A.; Sakamoto, K.; Ryoo, R.; Terasaki, O. *Prog. Solid State Chem.* **2014**, *42*, 1-21.

(5) Zhang, T.; Corma, A.; Schüth, F. *Catal. Today* **2014**, *234*, 1.

(6) Galeano Nunez, D. C.; Meier, J. C.; Soorholtz, M.; Bongard, H.-J.; Baldizzone, C.; Mayrhofer, K. J. J.; Schüth, F. *ACS Catal.* **2014**, *4*, 3856-3868.

(7) Käldström, M.; Meine, N.; Farès, C.; Schüth, F.; Rinaldi, R. *Green Chem.* **2014**, *7*, 3528-3538.

(8) Bellussi, G.; Caro, J.; Kärger, J.; Schüth, F.; Stöcker, M.; Weitkamp, J. *Microporous Mesoporous Mater.* **2014**, *184*, 70-71.

(9) Gu, D.; Jia, C.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Appl. Catal, B* **2014**, *152-153*, 11-18.

(10) Bazula, P.; Arnal, P.; Galeano Nunez, D. C.; Zibrowius, B.; Schmidt, W.; Schüth, F. *Microporous Mesoporous Mater.* **2014**, *200*, 317-325.

(11) Galeano Nunez, D. C.; Baldizzone, C.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Meier, J. C.; Mayrhofer, K. J. J.; Schüth, F. *Adv. Funct. Mater.* **2014**, *24*, 220-232.

(12) Wang, G.; Hilgert, J.; Richter, F.; Wang, F.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Schüth, F. *Nat. Mater.* **2014**, *13*, 293-300.

(13) Loerbroks, C.; van Rijn, J.; Ruby, M.-P.; Tong, Q.; Schüth, F.; Thiel, W. *Chem.-Eur. J.* **2014**, *20*, 12298-12309.

(14) Schüth, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8599-8604.

(15) Schüth, F.; Rinaldi, R.; Meine, N.; Käldström, M.; Hilgert, J.; Kaufman-Rechulski, M. D. *Special Issue of the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013)* **2014**, *234*, 24-30.

(16) Käldström, M.; Meine, N.; Farès, C.; Rinaldi, R.; Schüth, F. *Green Chem.* **2014**, *16*, 2454-2462.

(17) Meier, J. C.; Galeano Nunez, D. C.; Katsounaros, I.; Witte, J.; Bongard, H.-J.; Topalov, A. A.; Baldizzone, C.; Mezzavilla, S.; Schüth, F.; Mayrhofer, K. J. J. *Beilstein J. Nanotech.* **2014**, *5*, 44-67.

(18) Trotus, I.-T.; Zimmermann, T.; Schüth, F. *Chem. Rev.* **2014**, *114*, 1761-1782.

(19) Schüth, F.; Gu, D. *Chem. Soc. Rev.* **2014**, *43*, 313-344.

(20) Schüth, F. *Chem. Mater.* **2014**, *26*, 423-434.

(21) Wang, F.; Mielby, J.; Richter, F. H.; Wang, G.; Prieto, G.; Kasama, T.; Weidenthaler, C.; Bongard, H.-J.; Kegnæs, S.; Fürstner, A.; Schüth, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8645-8648.

(22) Zhang, A.; Coma, A.; Schüth, F. *Chin. J. Catal.* **2014**, *35*, 601-601.

(23) Schüth, F.; Eichel, R.-A. *Phys. J.* **2014**, *13*, 31-36.

(24) Auer, A. A.; Cap, S.; Antonietti, M.; Cherevko, S.; Deng, X.; Papakonstantinou, G.; Sundmacher, K.; Brüller, S.; Antonyshy, I.; Dimitratos, N.; Davis, R. J.; Fechler, N.; Freakley, S.; Grin, Y.; Gunnoe, B. T.; Haj-Hariri, H.; Hutchings, G.; Liang, H.; Mayrhofer, K. J. J.; Müllen, K.; Neese, F.; Ranjan, C.; Sankar, M.; Schlögl, R.; Schüth, F.; Spanos, I.; Stratmann, M.; Tüysüz, H.; Vidakovic-Koch, T.; Yi, Y.; Zangari, G. *Green* **2015**, *5*, 7-21.

(25) Deng, X.; Dodekatos, G.; Pupovac, K.; Weidenthaler, C.; Schmidt, W.; Schüth, F.; Tüysüz, H. *ChemCatChem* **2015**, *7*, 3832-3837.

(26) Lu, J.; Zhang, J.; Jiao, C.; Megarajan, S. K.; Gu, D.; Yang, G.; Jiang, H.; Jia, C.; Schüth, F. *Chin. Sci. Bull.* **2015**, *60*, 1108-1113.

(27) Gu, D.; Jia, C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W. N.; Schüth, F. *J. Am. Chem. Soc.* **2015**, *137*, 11855-12160.

(28) Passas-Lagos, E.; Schüth, F. *Langmuir* **2015**, *31*, 7749-7757.

(29) Prieto, G.; Schüth, F. *J. Catal.* **2015**, *328*, 59-71.

(30) Mezzavilla, S.; Baldizzone, C.; Mayrhofer, K. J. J.; Schüth, F. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12914-12922.

(31) Gu, D.; Li, W.; Wang, F.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao, D.; Schüth, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 7060-7064.

(32) Kaufman-Rechulski, M. D.; Käldström, M.; Richter, U.-B.; Schüth, F.; Rinaldi, R. *Ind. Eng. Chem. Res.* **2015**, *54*, 4581-4592.

(33) Lim, I.; Schrader, W.; Schüth, F. *Chem. Mater.* **2015**, *27*, 3088-3095.

(34) Tüysüz, H.; Schüth, F.; Zhi, L. J.; Muellen, K.; Comotti, M. *ChemCatChem* **2015**, *7*, 1453-1459.

(35) Trotus, I.-T.; Zimmermann, T.; Duyckaerts, N.; Geboers, J.; Schüth, F. *Chem. Commun.* **2015**, *51*, 7124-7127.

(36) Prieto, G.; Schüth, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 3222-3239.

(37) Guo, Y.; Gu, D.; Jin, Z.; Du, P.-P.; Si, R.; Tao, J.; Xu, W.-Q.; Huang, Y.-Y.; Senanayake, S.; Song, Q.-S.; Jia, C.-J.; Schüth, F. *Nanoscale* **2015**, *7*, 4920-4928.

(38) Baldizzone, C.; Mezzavilla, S.; Hodnik, N.; Zeradjanin, A. R.; Kostka, A.; Schüth, F.; Mayrhofer, K. J. J. *Chem. Commun.* **2015**, *51*, 1226-1229.

(39) Ausfelder, F.; Beilmann, C.; Bertau, M.; Braeuninger, S.; Heinzel, A.; Hoer, R.; Koch, W.; Mahlendorf, F.; Metzelthin, A.; Peuckert, M.; Plass, L.; Raeuchle, K.; Reuter, M.; Schaub, G.; Schiebahn, S.; Schwab, E.; Schüth, F.; Stolten, D.; Tessmer, G.; Wagemann, K.; Ziegahn, K.-F. *Chem. Ing. Tech.* **2015**, *87*, 17-89.

(40) Duyckaerts, N.; Trotus, I.-T.; Nese, V.; Swertz, A.-C.; Auris, S.; Wiggers, H.; Schüth, F. *ChemCatChem* **2015**, *7*, 2891-2896.

(41) Wang, G.; Cao, Z.; Gu, D.; Pfänder, N.; Swertz, A.-C.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Rinaldi, R.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 8850-8855.

(42) Wang, G.; Deng, X.; Gu, D.; Chen, K.; Tüysüz, H.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 11101-11105.

(43) Zimmermann, T.; Soorholtz, M.; Bilke, M.; Schüth, F. *J. Am. Chem. Soc.* **2016**, *138*, 12395-12400.

(44) Castro, M.; Haouas, M.; Lim, I.; Bongard, H.-J.; Schüth, F.; Taulelle, F.; Karlsson, G.; Alfredsson, V.; Breyneart, E.; Kirschhock, C. E. A.; Schmidt, W. *Chem.-Eur. J.* **2016**, *22*, 15307-15319.

(45) Prieto, G.; Tüysüz, H.; Duyckaerts, N.; Knossalla, J.; Wang, G.; Schüth, F. *Chem. Rev.* **2016**, *116*, 14056-14119.

(46) Polymeros, G.; Baldizzone, C.; Geiger, S.; Grote, J. P.; Knossalla, J.; Mezzavilla, S.; Keeley, G. P.; Cherevko, S.; Zeradjanin, A. R.; Schüth, F.; Mayrhofer, K. J. J. *Electrochim. Acta* **2016**, *211*, 744-753.

(47) Richter, F. H.; Sahraoui, L.; Schüth, F. *Chem. - Eur. J.* **2016**, *22*, 13563-13574.

(48) Ruby, M.-P.; Schüth, F. *Green Chem.* **2016**, *11*, 3422-3429.

(49) Wang, F.; Buchel, R.; Savitsky, A.; Zalibera, M.; Widmann, D.; Pratsinis, S. E.; Lubitz, W.; Schüth, F. *ACS Catal.* **2016**, *6*, 3520-3530.

(50) Knossalla, J.; Mezzavilla, S.; Schüth, F. *New J. Chem.* **2016**, *40*, 4361-4366.

(51) Gu, D.; Tseng, J.-C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Soulimani, F.; Weckhuysen, B. M.; Schüth, F. *J. Am. Chem. Soc.* **2016**, *138*, 9572-9880.

(52) Duyckaerts, N.; Trotus, I.-T.; Swertz, A.-C.; Schüth, F.; Prieto, G. *ACS Catal.* **2016**, *6*, 4229-4238.

(53) Lu, A. H.; Zhang, X.-Q.; Sun, Q.; Zhang, Y.; Song, Q.; Schüth, F.; Chen, C.; Cheng, F. *Nano Res.* **2016**, *9*, 1460-1469.

(54) Soorholtz, M.; Jones, L. C.; Samuelis, D.; Weidenthaler, C.; White, R. J.; Titirici, M.-M.; Cullen, D. A.; Zimmermann, T.; Antonietti, M.; Maier, J.; Palkovits, R.; Chmelka, B. F.; Schüth, F. *ACS Catal.* **2016**, *6*, 2332-2340.

(55) Schüth, F.; *Angew. Chem., Int. Ed.* **2016**, *55*, 14878-14879

(56) Mezzavilla, S.; Baldizzone, C.; Swertz, A.-C.; Hodnik, N.; Pizzutilo, E.; Polymeros, G.; Keeley, G.; Knossalla, J.; Heggen, M.; Mayrhofer, K.; Schüth, F. *ACS Catal.* **2016**, *6*, 8058-8068

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(57) Krech, D.; Zibrowius, B.; Weidenthaler, C.; Felderhoff, M. *Eur. J. Inorg. Chem.* **2014**, *33*, 5683-5688.

(58) Urbanczyk, R.; Peinecke, K.; Felderhoff, M.; Hauschild, K.; Kersten, W.; Peil, S.; Bathen, D. *Int. J. Hydrogen Energy* **2014**, *39*, 17118-17128.

(59) Hu, J.; Witter, R.; Shao, H.; Felderhoff, M.; Fichtner, M. *J. Mater. Chem. A* **2014**, *2*, 66-72.

(60) Ley, M. B.; Meggouh, M.; Moury, R.; Peinecke, K.; Felderhoff, M. *Materials* **2015**, *8*, 5891-5921.

(61) Bernert, T.; Krech, D.; Kockelmann, W.; Felderhoff, M.; Frankcombe, T. J.; Weidenthaler, C. *Eur. J. Inorg. Chem.* **2015**, *2015*, 5545-5550.

(62) Leon, A.; Finck, N.; Rothe, J.; Felderhoff, M.; Fichtner, M. *J. Phys. Chem. C* **2015**, *119*, 15810-15815.

(63) Shao, H.; Felderhoff, M.; Weidenthaler, C. *J. Phys. Chem. C* **2015**, *119*, 2341-2348.

(64) Moury, R.; Hauschild, K.; Kersten, W.; Ternieden, J.; Felderhoff, M.; Weidenthaler, C. *J. Appl. Crystallogr.* **2015**, *45*, 79-84.

(65) Wietelmann, U.; Felderhoff, M.; Rittmeyer, P. In *Ullmann's Encyclopedia of Industrial Chemistry, 100 Years*; Wiley-VCH - Wiley Online Library: Weinheim, **2016**; pp 1-36.

(66) Ley, M. B.; Bernert, T.; Ruiz-Fuertez, J.; Goddard, R.; Farès, C.; Weidenthaler, C.; Felderhoff, M. *Chem. Commun.* **2016**, *52*, 11649-11652.

(67) Cao, Z.; Ouyang, L.; Wang, H.; Liu, J.; Sun, L.; Felderhoff, M.; Zhu, M. *Int. J. Hydrogen Energy* **2016**, *41*, 11242-11253.

(68) Urbanczyk, R.; Peinecke, K.; Meggouh, M.; Minne, P.; Peil, S.; Bathen, D.; Felderhoff, M. *J. Power Sources* **2016**, *324*, 589-597.

(69) Bernert, T.; Ley, M. B.; Ruiz-Fuertes, J.; Fischer, M.; Felderhoff, M.; Weidenthaler, C. *Acta Crystallogr. Sect. B* **2016**, *72*, 232-240.

(70) Sheppard, D. A.; Paskevicius, M.; Humphries, T. D.; Felderhoff, M.; Capurso, G.; Bellosta von Colbe, J.; Dornheim, M.; Klassen, T.; Ward, P. A.; Teprovich, J. A.; Corgnale, C.; Zidan, R.; Grant, D. M.; Buckley, C. E. *Appl. Phys. A* **2016**, *122*, 395/1-15.

(71) Urbanczyk, R.; Meggouh, M.; Moury, R.; Peinecke, K.; Peil, S.; Felderhoff, M. *Appl. Phys. A* **2016**, *122*, 315/1-5.

(72) Crivello, J.-C.; Denys, R. V.; Dornheim, M.; Felderhoff, M.; Grant, D. M.; Huot, J.; Jensen, T. R.; de Jongh, P.; Latroche, M.; Walker, G. S.; Webb, C. J.; Yartys, V. A. *Appl. Phys. A* **2016**, *122*, 85/1-17.

Marlow Group

(73) Muldarisnur, M.; Marlow, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8761-8764.

(74) Marlow, F.; Hullermann, A.; Messmer, L. *Adv. Mater.* **2015**, *27*, 2447-2452.

(75) Deng, T. S.; Bongard, H.-J.; Marlow, F. *Mater. Chem. Phys.* **2015**, *162*, 548-554.

(76) Muldarisnur, M.; Marlow, F. *J. Nonlinear Opt. Phys. Mater.* **2016**, *25*, 1650015/1-12.

(77) Marlow, F.; Muldarisnur, M. In *Proc. of SPIE 9885, Photonic Crystal Materials and Devices XII*; **2016**, 98850S/1-7

Prieto Group

(21) Wang, F.; Mielby, J.; Richter, F. H.; Wang, G.; Prieto, G.; Kasama, T.; Weidenthaler, C.; Bongard, H.-J.; Kegnæs, S.; Fürstner, A.; Schüth, F. *Angew. Chem., Int. Ed.* **2014**, *53,* 8645-8648.

(29) Prieto, G.; Schüth, F. *J. Catal.* **2015**, *328*, 59-71.

(36) Prieto, G.; Schüth, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 3222-3239.

(45) Prieto, G.; Tüysüz, H.; Duyckaerts, N.; Knossalla, J.; Wang, G.; Schüth, F. *Chem. Rev.* **2016,** *116*, 14056-14119.

(52) Duyckaerts, N.; Trotus, I.-T.; Swertz, A.-C.; Schüth, F.; Prieto, G. *ACS Catal.* **2016**, *6*, 4229-4238.

(78) Gommes, C. J.; Prieto, G.; Zecevic, J.; Vanhalle, M.; Goderis, B.; de Jong, K. P.; de Jongh, P. E. *Angew. Chem., Int. Ed.* **2015**, *54*, 11804-11808.

(79) Prieto, G.; De Mello, M. I. S.; Concepcion, P.; Murciano, R.; Pergher, S. B. C.; Martinez, A. *ACS Catal.* **2015**, *5*, 3323-3335.

(80) Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Llabres i Xamena, F. X.; Gascon, J. *Nat. Mater.* **2015**, *14*, 48-55.

(81) Van den Berg, R.; Prieto, G.; Korpershoek, G.; van der Wal, L. I.; van Bunningen, A. J.; Lægsgaard-Jørgensen, S.; de Jongh, P. E.; de Jong, K. P. *Nat. Commun.* **2016**, *7*, 13057/1-7.

(82) Gommes, C. J.; Prieto, G.; de Jongh, P. E. *J. Phys. Chem. C* **2016**, *120*, 1488-1506.

Schmidt Group

(9) Gu, D.; Jia, C.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Appl. Catal., B* **2014**, *152-153*, 11-18.

(10) Bazula, P.; Arnal, P.; Galeano Nunez, D. C.; Zibrowius, B.; Schmidt, W.; Schüth, F. *Microporous Mesoporous Mater.* **2014**, *200*, 317-325.

(25) Deng, X.; Dodekatos, G.; Pupovac, K.; Weidenthaler, C.; Schmidt, W.; Schüth, F.; Tüysüz, H. *ChemCatChem* **2015**, *7*, 3832-3837.

(27) Gu, D.; Jia, C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W. N.; Schüth, F. *J. Am. Chem. Soc.* **2015**, *137*, 11855-12160.

(31) Gu, D.; Li, W.; Wang, F.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao, D.; Schüth, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 7060-7064.

(41) Wang, G.; Cao, Z.; Gu, D.; Pfänder, N.; Swertz, A.-C.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Rinaldi, R.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 8850-8855.

(42) Wang, G.; Deng, X.; Gu, D.; Chen, K.; Tüysüz, H.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 11101-11105.

(44) Castro, M.; Haouas, M.; Lim, I.; Bongard, H.-J.; Schüth, F.; Taulelle, F.; Karlsson, G.; Alfredsson, V.; Breyneart, E.; Kirschhock, C. E. A.; Schmidt, W. *Chem.-Eur. J.* **2016**, *22*, 15307-15319.

(51) Gu, D.; Tseng, J.-C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Soulimani, F.; Weckhuysen, B. M.; Schüth, F. *J. Am. Chem. Soc.* **2016**, *138*, 9572-9880.

(83) Castro, M.; Haouas, M.; Taulelle, F.; Lim, I.; Breynaert, E.; Brabants, G.; Kirschhock, C. E. A.; Schmidt, W. *Microporous Mesoporous Mater.* **2014**, *189*, 158-162.

(84) Verheyen, E.; Joos, L.; Martineau, C.; Dawson, C. J.; Weidenthaler, C.; Schmidt, W.; Yuan, R.; Breynaert, E.; van Speybroeck, V.; Waroquier, M.; Taulelle, F.; Treacy, M. M. J.; Martens, J. A.; Kirschhock, C. E. A. *Mater. Horiz.* **2014**, *1*, 582-587.

(85) Busch, M.; Schmidt, W.; Migunov, V.; Beckel, A.; Notthoff, C.; Kompch, A.; Bergmann, U.; Winterer, M.; Atakan, B. *Appl. Catal. B* **2014**, *160-161*, 641-650.

(86) Deng, X.; Schmidt, W.; Tüysüz, H. *Chem. Mater.* **2014**, *26*, 6127-6134.

(87) Sager, U.; Däubner, E.; Asbach, C.; Bathen, D.; Schmidt, F.; Weidenthaler, C.; Tseng, J. C.; Schmidt, W. *Gefahrstoff.-Reinhalt.-Luft* **2014**, No. 5, 181-184.

(88) Tseng, J.-C.; Schmidt, W.; Sager, U.; Däubner, E.; Pommerin, A.; Weidenthaler, C. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12282-12291.

(89) Sager, U.; Däubner, E.; Bathen, D.; Schmidt, W.; Weidenthaler, C.; Tseng, J.-C.; Pommerin, A. *Gefahrstoff.-Reinhalt.-Luft* **2016**, *76*, 338-343.

(90) Sager, U.; Däubner, E.; Bathen, D.; Asbach, C.; Schmidt, F.; Tseng, J.-C.; Pommerin, A.; Weidenthaler, C.; Schmidt, W. *Adsorpt. Sci.Technol.* **2016**, *34*, 307-319.

Tüysüz Group

(24) Auer, A. A.; Cap, S.; Antonietti, M.; Cherevko, S.; Deng, X.; Papakonstantinou, G.; Sundmacher, K.; Brüller, S.; Antonyshy, I.; Dimitratos, N.; Davis, R. J.; Fechler, N.; Freakley, S.; Grin, Y.; Gunnoe, B. T.; Haj-Hariri, H.; Hutchings, G.; Liang, H.; Mayrhofer, K. J. J.; Müllen, K.; Neese, F.; Ranjan, C.; Sankar, M.; Schlögl, R.; Schüth, F.; Spanos, I.; Stratmann, M.; Tüysüz, H.; Vidakovic-Koch, T.; Yi, Y.; Zangari, G. *Green*, **2015**, *5*, 7-21.

(25) Deng, X.; Dodekatos, G.; Pupovac, K.; Weidenthaler, C.; Schmidt, W.; Schüth, F.; Tüysüz, H. *ChemCatChem* **2015**, *7*, 3832-3837.

(34) Tüysüz, H.; Schüth, F.; Zhi, L. J.; Muellen, K.; Comotti, M. *ChemCatChem* **2015**, *7*, 1453-1459.

(42) Wang, G.; Deng, X.; Gu, D.; Chen, K.; Tüysüz, H.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 11101-11105.

(45) Prieto, G.; Tüysüz, H.; Duyckaerts, N.; Knossalla, J.; Wang, G.; Schüth, F. *Chem. Rev.* **2016,** *116*, 14056-14119.

(86) Deng, X.; Schmidt, W.; Tüysüz, H. *Chem. Mater.* **2014**, *26*, 6127-6134.

(91) Piao, L.; Chen, X.; Li, Y.; Tüysüz, H. *Catal. Today* **2014**, *225*, 1-1.

(92) Grewe, T.; Deng, X.; Tüysüz, H. *Chem. Mater.* **2014**, *26*, 3162-3168.

(93) Grewe, T.; Deng, X.; Tüysüz, H. *Chem.-Eur. J.* **2014**, *20*, 7692-7697.

(94) Parsons-Moss, T.; Tüysüz, H.; Wang, D.; Jones, S.; Olive, D.; Nitsche, H. *Radiochim. Acta* **2014**, *102*, 489-504.

(95) Grewe, T.; Meier, K.; Tüysüz, H. *Catal. Today* **2014**, *225*, 142-148.

(96) Deng, X.; Tüysüz, H. *ACS Catal.* **2014**, *4*, 3701-3714.

(97) Schünemann, S.; Dodekatos, G.; Tüysüz, H. *Chem. Mater.* **2015**, *27*, 7743-7750.

(98) Grewe, T.; Tüysüz, H. *ACS Appl. Mater. Interfaces* **2015**, *7*, 23153-23162.

(99) Chen, K.; Tüysüz, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 13806-13810.

(100) Grewe, T.; Tüysüz, H. *ChemSusChem* **2015**, *8*, 3084-3091.

(101) Grewe, T.; Meggouh, M.; Tüysüz, H. *Chem.-Asian J.* **2016**, *11*, 22-42.

(102) Chan, C. K.; Tüysüz, H.; Braun, A.; Ranjan, C.; La Mantia, F.; Miller, B. K.; Zhang, L.; Crozier, P. A.; Haber, J. A.; Gregoire, J. M.; Park, H. S.; Batchellor, A. S.; Trotochaud, L.; Boettcher, S. W. *Top. Curr. Chem.* **2016**, *371*, 253-324.

(103) Dodekatos, G.; Schünemann, S.; Tüysüz, H. *Top. Curr. Chem.* **2016**, *371*, 215-252.

(104) Deng, X.; Chan, C.; Tüysüz, H. *ACS. Appl. Mater. Interfaces*, **2016**, *8*, 32488-32495.

(105) Dodekatos, G.; Tüysüz, H. *ChemCatChem*, DOI: 10.1002/cctc.201601219.

(106) Deng, X.; Chen, K.; Tüysüz, H. *Chem. Mater.* **2016**, in press, DOI:10.1021/acs.chemmater.6b02645.

(107) Dodekatos, G.; Tüysüz, H. *Catal. Sci. Technol.* **2016**, *6*, 7307-7315.

(108) Schünemann, S.; Chen, K.; Brittman, S.; Garnett, E.; Tüysüz, H. *ACS Appl. Mater. Interfaces* **2016**, *8*, 25489-25495.

(109) Konkena, B.; junge Puring, K.; Sinev, I.; Piontek, S.; Khavryuchenko, O.; Durholt, J. P.; Schmid, R.; Tüysüz, H.; Muhler, M.; Schuhmann, W.; Apfel, U.-P. *Nat. Commun.* **2016**, *7*, 12269-.

(110) Chen, K.; Deng, X.; Goddard, R.; Tüysüz, H. *Chem. Mater.* **2016**, *28*, 5530-5537.

(111) Grewe, T.; Tüysüz, H. *ChemNanoMat* **2016**, *2*, 274-280.

(112) Deng, X.; Bongard, H.-J.; Chan, C. K.; Tüysüz, H. *ChemSusChem* **2016**, *9*, 409-415.

(113) Grewe, T.; Tüysüz, H. *J. Mater. Chem. A* **2016**, *4*, 3007-3017.

(114) Grewe, T.; Yang, T.; Tüysüz, H.; Chan, C. K. *J. Mater. Chem. A* **2016**, *4*, 2837-2841.

Weidenthaler Group

(09) Gu, D.; Jia, C.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Applied Catalysis B* **2014**, *152-153*, 11-18.

(11) Galeano Nunez, D. C.; Baldizzone, C.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Meier, J. C.; Mayrhofer, K. J. J.; Schüth, F. *Adv. Funct. Mater.* **2014**, *24*, 220-232.

(12) Wang, G.; Hilgert, J.; Richter, F.; Wang, F.; Bongard, H.-J.; Spliethoff, B.; Weidenthaler, C.; Schüth, F. *Nat. Mater.* **2014**, *13*, 293-300.

(21) Wang, F.; Mielby, J.; Richter, F. H.; Wang, G.; Prieto, G.; Kasama, T.; Weidenthaler, C.; Bongard, H.-J.; Kegnæs, S.; Fürstner, A.; Schüth, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8645-8648.

(25) Deng, X.; Dodekatos, G.; Pupovac, K.; Weidenthaler, C.; Schmidt, W.; Schüth, F.; Tüysüz, H. *ChemCatChem* **2015**, *7*, 3832-3837.

(27) Gu, D.; Jia, C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W. N.; Schüth, F. *J. Am. Chem. Soc.* **2015**, *137*, 11855-12160.

(31) Gu, D.; Li, W.; Wang, F.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao, D.; Schüth, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 7060-7064.

(41) Wang, G.; Cao, Z.; Gu, D.; Pfänder, N.; Swertz, A.-C.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Rinaldi, R.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 8850-8855.

(42) Wang, G.; Deng, X.; Gu, D.; Chen, K.; Tüysüz, H.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 11101-11105.

(51) Gu, D.; Tseng, J.-C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.; Soulimani, F.; Weckhuysen, B. M.; Schüth, F. *J. Am. Chem. Soc.* **2016**, *138*, 9572-9880.

(54) Soorholtz, M.; Jones, L. C.; Samuelis, D.; Weidenthaler, C.; White, R. J.; Titirici, M.-M.; Cullen, D. A.; Zimmermann, T.; Antonietti, M.; Maier, J.; Palkovits, R.; Chmelka, B. F.; Schüth, F. *ACS Catal.* **2016**, *6*, 2332-2340.

(57) Krech, D.; Zibrowius, B.; Weidenthaler, C.; Felderhoff, M. *Eur. J. Inorg. Chem.* **2014**, *33*, 5683-5688.

(61) Bernert, T.; Krech, D.; Kockelmann, W.; Felderhoff, M.; Frankcombe, T. J.; Weidenthaler, C. *Eur. J. Inorg. Chem.* **2015**, *2015*, 5545-5550

(63) Shao, H.; Felderhoff, M.; Weidenthaler, C. *J. Phys. Chem. C* **2015**, *119*, 2341-2348.

(64) Moury, R.; Hauschild, K.; Kersten, W.; Ternieden, J.; Felderhoff, M.; Weidenthaler, C. *J. Appl. Crystallogr.* **2015**, *45*, 79-84.

(66) Ley, M. B.; Bernert, T.; Ruiz-Fuertez, J.; Goddard, R.; Farès, C.; Weidenthaler, C.; Felderhoff, M. *Chem. Commun.* **2016**, *52*, 11649-11652.

(69) Bernert, T.; Ley, M. B.; Ruiz-Fuertes, J.; Fischer, M.; Felderhoff, M.; Weidenthaler, C. *Acta Crystallogr. Sect. B* **2016**, *72*, 232-240.

(84) Verheyen, E.; Joos, L.; Martineau, C.; Dawson, C. J.; Weidenthaler, C.; Schmidt, W.; Yuan, R.; Breynaert, E.; van Speybroeck, V.; Waroquier, M.; Taulelle, F.; Treacy, M. M. J.; Martens, J. A.; Kirschhock, C. E. A. *Mater. Horiz.* **2014**, *1*, 582-587.

(87) Sager, U.; Däubner, E.; Asbach, C.; Bathen, D.; Schmidt, F.; Weidenthaler, C.; Tseng, J. C.; Schmidt, W. *Gefahrstoffe Reinhaltung der Luft / Air Quality Control* **2014**, *5*, 181-184.

(88) Tseng, J.-C.; Schmidt, W.; Sager, U.; Däubner, E.; Pommerin, A.; Weidenthaler, C. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12282-12291.

(89) Sager, U.; Däubner, E.; Bathen, D.; Schmidt, W.; Weidenthaler, C.; Tseng, J.-C.; Pommerin, A. *Gefahrstoff.-Reinhalt.-Luft* **2016**, *76*, 338-343.

(90) Sager, U.; Däubner, E.; Bathen, D.; Asbach, C.; Schmidt, F.; Tseng, J.-C.; Pommerin, A.; Weidenthaler, C.; Schmidt, *W. Adsorp. Sci. Technol.* **2016**, 34, 307-319.

(118) Tagliazucca, V.; Leoni, M.; Weidenthaler, C. *Phys. Chem. Chem. Phys.* **2014**, *16*, 21882-21882.

(119) Mielby, J.; Abildstrøm, J. O.; Wang, F.; Kasama, T.; Weidenthaler, C.; Kegnæs, S. *Angew. Chem., Int. Ed.* **2014**, *126*, 12721-12724.

(120) Tagliazucca, V.; Leoni, M.; Weidenthaler, C. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6182-6188.

(121) Ji, N.; Wang, X.; Weidenthaler, C.; Spliethoff, B.; Rinaldi, R. *ChemCatChem* **2015**, *7*, 960-966.

(122) Gu, Y.-Q.; Fu, X.-P.; Du, P.-P.; Gu, D.; Jin, Z.; Huang, Y.-Y.; Si, R.; Zheng, L.-Q.; Song, Q.-S.; Jia, C.-J.; Weidenthaler, C. *J. Phys. Chem. C* **2015**, *119*, 17102-17110.

(123) Callini, E.; Atakli, Z. O. K.; Hauback, B. C.; Orimo, S.; Jensen, C.; Dornheim, M.; Grant, D.; Cho, Y. W.; Chen, P.; Hjorvarsson, B.; de Jongh, P.; Weidenthaler, C.; Baricco, M.; Paskevicius, M.; Jensen, T. R.; Bowden, M. E.; Autrey, T. S.; Zuettel, A. *Appl. Phys. A* **2016**, *122*:353.

Schüth Group / Rinaldi

(7) Käldström, M.; Meine, N.; Farès, C.; Schüth, F.; Rinaldi, R. *Green Chem.* **2014**, *16*, 3528-3538

(15) Schüth, F.; Rinaldi, R.; Meine, N.; Käldström, M.; Hilgert, J.; Kaufman Rechulski, M. D. *Catal. Today* **2014**, *234*, 24-30.

(16) Käldström, M.; Meine, N.; Farès, C.; Rinaldi, R.; Schüth, F. *Green Chem.* **2014**, *16*, 2454-2462.

(32) Kaufman Rechulski, M. D.; Käldström, M.; Richter, U.; Schüth, F.; Rinaldi, R. *Ind. Eng. Chem. Res.* **2015**, *54*, 4581-4592.

(41) Wang, G.-H.; Cao, Z.; Gu, D.; Pfänder, N.; Swertz, A.-C.; Spliethoff, B.; Bongard, H.-J.; Weidenthaler, C.; Schmidt, W.; Rinaldi, R.; Schüth, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 8850-8855.

(121) Ji, N.; Wang, X.; Weidenthaler, C.; Spliethoff, B.; Rinaldi, R. *ChemCatChem* **2015**, *7*, 960-966.

(124) Rinaldi, R. RSC EES Book Series **2014**, *74-98*.

(125) Ferrini, P.; Rinaldi, R. *Angew. Chem., Int. Ed.* **2014**, 53, 8634-8639.

(126) Rinaldi, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 8559-8560.

(127) Geboers, J.; Wang, X.; de Carvalho, A. B.; Rinaldi, R. *J. Mol. Catal. A: Chem.* **2014**, *388-389*, 106-115.

(128) de Oliveira, H. F. N.; Farès, C.; Rinaldi, R. *Chem. Sci.* **2015**, *6*, 5215-5224.

(129) de Oliveira, H. F. N.; Rinaldi, R. *ChemSusChem* **2015**, *8*, 1577-1584.

(130) Ferrini, P.; Rezende, C. A.; Rinaldi, R. *ChemSusChem* **2016**, *9*, DOI:10.1002/cssc.201601121.

(131) de Oliveira, H. F. N.; Clough, M.T.; Rinaldi, R. *ChemSusChem* **2016**, *9*, DOI:10.1002/cssc.201601108.

(132) Chesi, C.; de Castro, I. B. D.; Clough, M.T.; Ferrini, P.; Rinaldi, R. *ChemCatChem* ***2016***, *8*, 2079-2088.

(133) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijnincx, P. C. A.; Weckhuysen, B.M. *Angew. Chem., Int. Ed.* **2016**, *55*, 8164-8215.

(134) Wang, X.; Rinaldi, R. *Catal. Today* **2016**, *269*, 48-55.