2.3 Department of Heterogeneous Catalysis

Director:

Ferdi Schüth (born 1960)

Publications: 4, 5, 9, 11, 40, 52, 57, 58, 68, 79, 80, 97, 98, 99, 103, 104, 107, 108, 109, 110, 111, 112, 113, 126, 127, 128, 129,137, 146, 154, 159, 162, 172, 203, 204, 221, 223, 224, 226, 229, 244, 245, 250, 251, 252, 256, 263, 264, 269, 272, 274, 276, 277, 282, 302, 306, 307, 308, 313, 314, 316, 330, 331, 332, 345, 351, 352, 353, 354, 360, 369, 373, 379, 380, 390, 391, 394, 395, 396, 397, 427

Further group leaders:

An-Hui Lu (born 1972)

left the Institute in June 2009

Publications: 5, 57, 58, 162, 274, 306, 307, 308, 331, 352, 353, 354

Frank Marlow (born 1960)

Publications: 53, 82, 120, 194, 208, 212

Regina Palkovits (born 1980)

joined the Institute in January 2008

Publications: 73, 79, 97, 98, 99, 146, 223, 224, 225, 226, 341, 368, 369, 370, 371, 372, 373, 391, 408

Roberto Rinaldi (born 1979)

group leader since July 2009

Publications: 97, 98, 99, 242, 243, 244, 245, 328, 352, 359, 360, 370, 390, 391

Wolfgang Schmidt (born 1962)

Publications: 19, 46, 79, 100, 131, 132, 192, 226, 253, 254, 315, 331, 332, 352, 389, 394

Oliver Trapp (born 1973)

left the Institute in September 2008

Publications: 121, 122, 123, 124, 125, 163, 411

Other publications: 25, 44, 49, 50, 55, 56, 66, 81, 138, 148, 152, 160, 169, 175, 186, 199, 201, 211, 257, 296, 324, 346, 416

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

Other Activities / Committees

1995-1997	Managing Director of the Institute of Inorganic Chemistry, Frankfurt University
1995-2001	Coordinator of the DFG-Schwerpunktprogramm “Nanoporous Crystals”
1994	Member of the Dechema Arbeitsausschuss “Heterogene Katalyse”
1995-2005	Member of the Dechema Arbeitsausschuss “Zeolithe”
1996-2004	Member of the Dechema Arbeitsausschuss “Mikroreaktionstechnik”
1996-	Member of the Editorial Board, *Microporous Materials*
1998	Member of the Editorial Board, *Advanced Materials*
1998-2005	Chairman of the Dechema Arbeitsausschuss “Zeolithe”
1999-	Founder, Chairman of the Board and of the Scientific Advisory Board hte AG
1999-2005	Member of the Kuratorium, *Nachrichten aus der Chemie*
2000-	Member of the Dechema Board of Governors
2000-	Member of the Selection Committee for the Humboldt Award
2001-	Member of the IZA-Council
2001-	Chairman of the IZA Commission on Mesoporous Materials
2001-2006	Member of the Editorial Board, *Chemistry of Materials*
2002-	Member of the IMMA-Council
2002-2007	Member of the Selection Committee Heinz Maier-Leibniz Award
2003-2005	Managing Director of the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr
2003-2007	Member of the Deutsche Forschungsgemeinschaft Senate Commission for SFB
2003-2010	Chairman of the Selection Committee, Alexander von Humboldt Award
2003-	Member of the Editorial Board “QSAR-Combinatorial Science”
2003-	Member of the International Expert Commission Elitenetzwerk Bayern
2004-2008	Member of the Kuratorium Universität Duisburg-Essen
2004-	Member of the Editorial Board, *Chemical Communications*
2004-	Member of the Scientific Commission of the State of Niedersachsen
2004-	Member of the GDCh Board of Governors
2004-	Chairman of the Dechema Forschungsausschuss “Chemical Reaction Engineering”
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
2007-	Vice-President of the Deutsche Forschungsgemeinschaft (DFG)
2009-	Vice-Chairman of the Scientific Council of the Max Planck Society
2009-	Vice-Chairman of Dechema
2009-	Member of the Supervisory Board of the Karlsruhe Institute of Technology (KIT)

Research in the Department of Heterogeneous Catalysis

The department of Heterogeneous Catalysis has seen substantial personnel change over the last three years, which is, however, fully intended. While the Institute plans stability with respect to the heads of departments, the positions of most 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 guarantees the influx of new ideas and approaches on a regular basis, since leaving group leader positions are filled typically by scientists from outside. Continuity of the work is ascertained by the director of the department (F. Schüth) and few senior scientists on permanent positions, either as group leaders or staff scientists (F. Marlow, W. Schmidt, C. Weidenthaler).

Due to the high importance of restructuring our energy system, research in this direction is considered to be highly important by the director of the department. This has not led to a change in the general approach to catalysis, i.e. exploitation of porosity and nano-structuring. However, the target reactions which are being studied are more and more related to energy questions. Several of the research directions of the department have not drastically changed, but naturally evolved and flourished. These include investigations of fundamentals of solids formation, porous solids, nanostructured catalysts and optical properties of solids. But in addition to these, some new developments were initiated, which broadened the scope of the research. There are strongly intensified efforts in the field of biomass conversion, which are pursued in the groups of F. Schüth, R. Palkovits and R. Rinaldi, and a new activity in the group of F. Schüth on porous polymer catalysts, which is predominantly funded since 2010 by an ERC Advanced Grant. The activities in the field of ordered mesoporous materials have been downsized to some extent. It is felt that such materials have reached a certain degree of maturity and thus are now part of the regular toolbox of catalysis. Some challenges still remain, but the overall importance has decreased. The investigation of complex hydrides has shifted in focus: while previously this direction was dominated by the goal to find novel storage materials for applications in cars, primarily based on $NaAlH_4$ and partially driven by the long and substantial interaction with Opel, it is now oriented more towards fundamental questions of discovering new hydride materials.

Over the reporting period, altogether six groups were active in the department, although not all of them over the whole period. In fact, the only groups which were in full operation between 2008 and 2010 were the group of F. Schüth (director) and that of

F. Marlow. O. Trapp left the Institute in September 2008 to become a professor at Heidelberg University. He was succeeded by R. Palkovits, who, in turn, also moved on to a new challenge as a professor at RWTH Aachen in October 2010. However, she and her group will continue to pursue research in the Institute until approximately middle of 2011, since the lab space at RWTH is still being created. A potential successor of R. Palkovits has already been identified: H. Tüysüz had graduated from the group of F. Schüth in 2009 and is presently post-doc in the group of P. D. Yang at Berkeley. He has expressed interest in returning to Mülheim in 2011. A.-H. Lu was appointed professor at Dalian University of Technology in the middle of 2009. He was succeeded by R. Rinaldi, who had been a post-doc in the department before. R. Rinaldi has been awarded a Sofja Kovalevskaja prize in 2010 which makes him financially almost fully independent. Finally, due to the high quality research and his visible scientific profile, W. Schmidt was promoted to group leader in the reporting period, so that there are now five groups (including the one of the director) in the department. In addition to the groups listed above, B. Bogdanović who sadly passed away in 2010, was still associated with the department to support the work on hydrogen storage materials, while the day-to-day activities of the hydrogen storage team were coordinated by M. Felderhoff. Substantial independent research has also been carried out by C. Weidenthaler in the field of advanced XRD methods in catalysis research and J. Kornatowski, who has supplied tailored samples of specific molecular sieve crystals to a number of cooperating groups.

A major thrust of the department is development of novel synthetic methods for nano-structured materials with predominant applications in catalysis. A strong focus in the reporting period was placed on the combination of colloidal synthesis of nanoparticles, creation of defined pore systems and different templating concepts. This combination has allowed the development of catalysts structured at will on the nanoscale, in order to introduce novel functionality. This line of research has led to the synthesis of various complex composite catalysts which are, for instance, sinter stable, or are superparamagnetic, so that they can be magnetically separated and recycled. The expertise built up in this line of research has also led to the synthesis of other interesting materials, such as mesostructured magnetic oxides of different composition which were explored in cooperation with the Zabel-group at Bochum University. Also materials with interesting optical properties are synthesized and studied, and the group of F. Marlow has proved to be instrumental in obtaining deeper insight in the exciting properties of such systems. The activities in the field of optical materials have also repercussions on the catalysis oriented research, since a new line of work on photocatalysis is expected to develop over the next years.

Most of the reactions studied are now in the wider field of energy catalysis. There is a number of projects for the conversion of biomass to fuels and other value-added products, including hydrolytic and hydrogenolytic depolymerization of cellulose, and different sugar-transformation reactions, such as to hydroxymethylfurfural or different furan derivates. Moreover, R. Rinaldi is ramping up a program on lignin conversion, and glycerol as an abundant byproduct of Biodiesel fuel production is explored with respect to its catalytic conversion. Other energy-related projects are in the field of synthesis gas chemistry, methane activation via solid-catalyzed Periana-type chemistry, and ammonia decomposition for the generation of CO_x-free hydrogen as fuel cell feed.

While most of the general research themes pursued in the department are covered in the individual reports on the research areas, some of the activities do not fall into one of the categories. These include, for instance, studies on high throughput experimentation, in which some still lacking experimental techniques have been developed and artificial intelligence methods have been further explored. However, high throughput experimentation has become a routine tool by now, and thus no special report will be devoted to this topic. Results on such projects that do not fall into one of the research areas described can be found in the complete list of publications.

A powerful new analytical method, HR-SEM, in the microscopy group has boosted the capabilities of the department to obtain unprecedented insight in the structure of ordered mesoporous materials and other solid catalysts. In close collaboration with other analytical departments, in-situ XRD techniques were further developed and exploited in several projects, and the very interesting work on the use of ESI mass spectrometry for the study of nucleating solutions has been further pursued, especially adding MS-MS techniques to the toolbox in order to obtain structural information.

The groups of the department are not only participating in internal cooperations, but are also integrated in intensive external cooperation networks, either through formal or informal cooperation. These cooperations include an EU network of excellence (IDECAT), BMBF and AIF grants, integration into the nano-energy program at the University Duisburg-Essen, and participation of the department in DFG Schwerpunktprogrammen (priority programs) and Sonderforschungsbereichen (centers of excellence). Notably, the department is also a member of the cluster of excellence

(CoE) “Tailor-made fuels from biomass” at RWTH Aachen which proved to be a stepping stone for R. Palkovits, who is now professor in Aachen. The CoE is also highly important for R. Rinaldi, who runs a very successful project as part of the cluster. For the next round of proposals in the framework of the Excellence Initiative, the department is partner in one cluster proposal at the Universität Duisburg-Essen and two at the Ruhr-Universität Bochum.

In addition to the integration in bigger networks, there are many bilateral research projects between research groups, and funded cooperation projects with industrial companies. Especially fruitful was the cooperation with Osamu Terasaki, who was affiliated to the department as an Alexander von Humboldt Senior Award winner during the reporting period. This has enhanced the capabilities for high level electron microscopy analysis substantially. The department is also a node in the Max Planck International Research School SURMAT. The work of the members of the department has been recognized by a number of awards and distinctions, several of which contribute to the third-party funding of the activities. Most notable are the ERC Advanced Grant to F. Schüth (€ 1.76 M), the Robert Bosch Junior Professorship to R. Palkovits (€ 1 M) and the Sofja Kovalevskaja Award of R. Rinaldi (€ 1.54 M). Other awards to different members of the department are listed in a separate section.

2.3.1 Research Area “Understanding the Synthesis of Solid Catalysts”

(F. Schüth)

Involved: A. Kempter, I. Lim, B. B. Schaack, S. S. Wang

Objective: Understanding the fundamental processes during the synthesis of solids is essential for a rational design of catalysts. In this group of projects we develop the tools to study the early stages of solids formation from solution and apply them to problems of the department. This group of projects is of a rather fundamental character with a correspondingly long time scale.

Results: Electrospray Ionization Mass Spectrometry (ESI-MS) had already been discussed in the last report as a very powerful tool for the study of pre-nucleating and nucleating solutions. First time-resolved studies had been described in the last report. Since then, significant progress has been made, both with respect to insight in the systems studied and the methodology.

Germanium containing zeolites have been in the focus of the attention, as they have attracted very high interest due to the work of primarily the Corma-group who was successful in the synthesis of a number of highly interesting novel structures with ultra-large pores. In order to understand the formation and the relevant factors governing the synthesis of such materials, several germanium containing zeolites have been analyzed with ESI MS techniques. It was found that immediately before the detection of the first solid particles by light scattering, oligomers are present in solution that are also structural elements

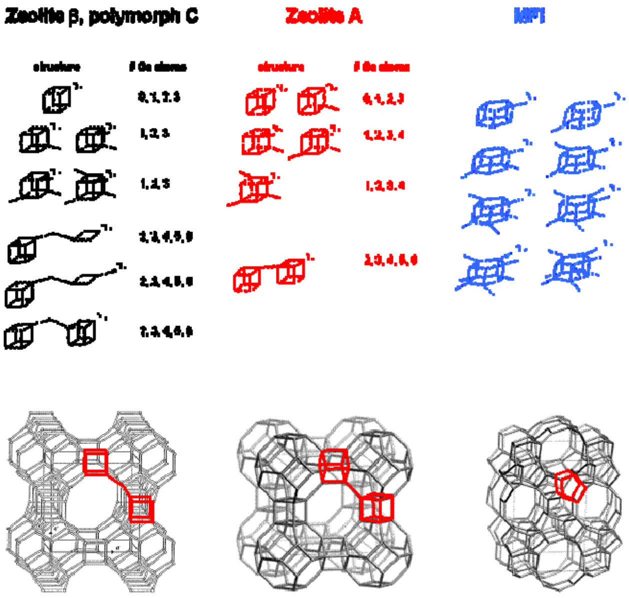

Fig. 1. Top: selected oligomeric species detected immediately before solids formation in different zeolite synthesis systems. For zeolite beta and zeolite A, several germanium atoms were found in the oligomers due to the high germanium content of the systems, in the MFI system, the germanium concentration is low, so that each oligomer contained one germanium atom at most. Bottom: sections from the corresponding structures, with characteristic elements highlighted in red.

in the final zeolite structures of the specific synthesis system (Figure 1). In the system which results in the formation of zeolite beta, double four-ring units bridged by a single silicate moiety were detected immediately before nucleation, for zeolite A-synthesis directly linked double four-rings were found, whereas in the synthesis of Ge-containing MFI-type material double five-ring units are present. While the double five-rings are not exactly secondary building units of MFI, the five-rings, which are characteristic for MFI-type materials are already formed in solution. These results demonstrate that building blocks found in the final structure of the zeolite are also favored species in solution, and nucleation of the solid seems to occur when the concentration of the relevant species has exceeded a certain concentration.

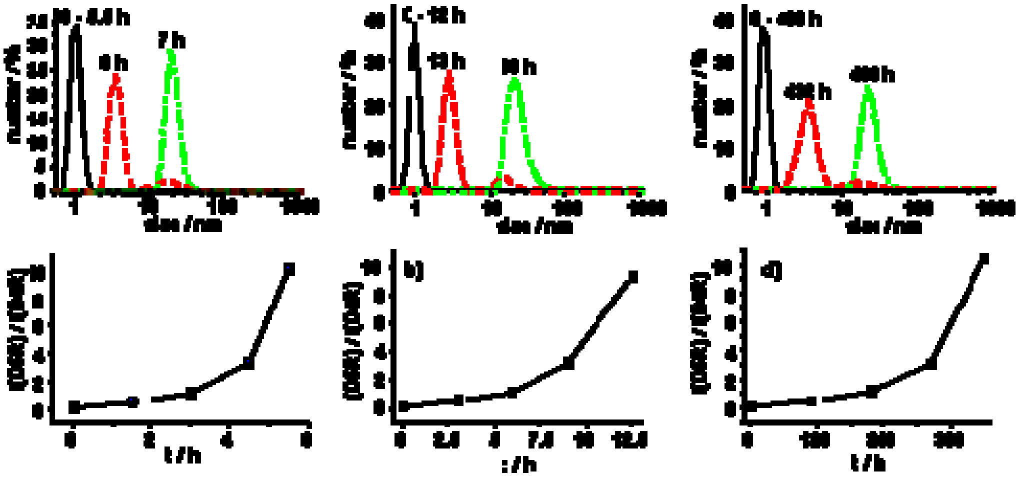

Fig. 2. Nucleation of Al-MFI at different temperatures (170°C left, 100°C middle, 40°C right). Top: particle size distribution determined by light scattering. Bottom: ratio between double-five ring silicate species and double-four ring silicate species over synthesis time determined by ESI MS.

This is even more convincingly seen in a study in which the formation of Al-MFI was studied at different temperatures. Depending on the temperature, the formation of the first solid (detected by light scattering) occurs at very different times, i.e. after only about 5 h at 170°C, after about 12 h at 100°C, and only after 400 h at 40°C. Interestingly, initially a high concentration of the stable cubic octamer silicate was formed under all conditions, but the concentration of this species decreased on expense of double five-ring species. At all temperatures, the first solid particles were detected by light scattering, when the ratio of double five-rings to double four-rings reached about 10 (Figure 2). This suggests that the double five-ring species is crucial for the formation of the MFI structure, and that solids formation requires a certain concentration of such species. The mysterious "induction time" observed in zeolite crystallization – and in the formation of other solids from solution – is thus necessary for the decisive species for crystallization to build up.

This analysis, however, required not only the determination of sum formula of the detected species which is straightforward in mass spectrometry, but also the elucidation of the structures of the species. This was achieved by MS-MS experiments, in which species of one mass were first isolated in an ion trap and fragmented by collisions with inert species. The mass resolved analysis of the formed fragments in a second mass filter then allows conclusions on the structures of the initial species. Using such methods, it was possible to obtain insight in the distribution of heteroelements in the different oligomers formed in solution. It could, for instance, be shown that the Loewenstein-rule (no Al-O-Al linkages in zeolites) was obeyed to a large extent for the solution species, but that a minor fraction of the alumosilicate oligomers in solution did in fact violate this rule. Germanium was found with a maximum number of three per cubic octamer, species with four germanium octamers were not detected.

EXAFS is routinely used in cooperation with the group of J. D. Grunwaldt for the study of catalyst formation. Especially the synthesis of copper nanoparticles was investigated in detail, using different synthetic routes. It could be shown that an identical low-temperature intermediate was formed, irrespective of the initial precursor, which explains the low influence of the precursor and the low extent of tuning which is possible in the synthesis of copper nanoparticles by the Bönnemann route. These experiments did not only give important hints for the synthesis of size controlled copper clusters, but also extended the range of possibilities of the EXAFS technique in this cooperation.

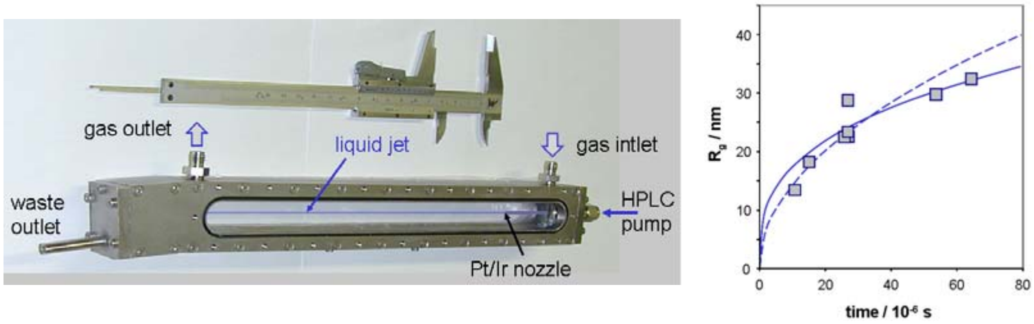

Fig. 3. Jet reactor for accessing extremely short precipitation times (left). The solution enters the chamber from the right, the synchrotron radiation beam passes perpendicularly through the transparent windows. Right: Particle radii calculated from the SAXS data at different reaction times for the injection of a 1 M Zn^{2+} solution in a 1/3 H_2S/N_2 atmosphere.

For accessing very short reaction times in the formation of solids, tubular reactor concepts were used already repeatedly in the past by the group. However, due to mixing problems, these approaches are typically restricted to time scales longer than several milliseconds. For the analysis of reactions which are faster, a jet reactor has been developed, in which a precursor solution is injected through a pinhole into a reactive gas atmosphere, in the case studied, a Zn^{2+} solution was injected into a H_2S atmosphere (Figure 3). Using synchrotron radiation, this setup allowed recording small angle scattering data at time scales down to several microseconds. It could be shown that on this time scale, ZnS formation is a diffusion controlled process, no obvious nucleation threshold was detected for the conditions studied.

Publications resulting from this research area: 4, 103, 250, 251, 252, 269, 394

External Funding: Deutsche Forschungsgemeinschaft (SFB 558); Leibniz Award

Cooperations: H. Amenitsch (Graz, AT); A. Corma (Valencia, ES); A. Erdem-Sentalar (Istanbul, TR); J. D. Grunwaldt (Zürich, CH); M. Lindén (Abo, FI); W. Schmidt, W. Schrader (Mülheim, DE)

2.3.2 Research Area "High Surface Area Materials" (F. Schüth)

Involved: P. A. Bazula, M. J. Benitez, T. Klasen, J. Kornatowski, W. C. Li, Y. Liu, Y. Meng, J. J. Nitz, F. Richter, E. L. Salabas, B. B. Schaack, M. Schwickardi, Q. Tong, H. Tüysüz, C. Weidenthaler

Objective: In this group of projects we are investigating and developing novel pathways for the synthesis of high surface area materials. The focus of the work is on oxides and carbon-based materials. The latter materials were, to a large extent, explored in the group of A.-H. Lu but after he took over the professor position at Dalian activities were reintegrated into the group of F. Schüth. Several projects are pursued in cooperation between these groups. The major synthetic methods still rely on different templating approaches, but also other techniques, such as sol-gel synthesis, are being used. While the main reason for the synthesis of high surface area materials is catalysis, other application areas, such as sorption or magnetism, are being explored as well. There is a natural interaction between the projects in this research area with the field of nanoengineered catalysts, since many of the high surface area materials synthesized are subsequently used as components for the fabrication of designed composites.

Results: Most activities related to zeolites have now been transferred to the group of W. Schmidt and will be subject of a separate report. Several projects are continuing in cooperation between the two groups. For instance, size-tailored zeolites were synthesized in close collaboration with him and then used for the dehydration of glycerol to acrolein. It was clearly shown that the reaction is strongly mass transfer limited. Optimum zeolites are thus those with high acid site concentration and small particle sizes.

Ordered mesoporous materials, synthesized either by solution processes or by nanocasting, are still subject of intensive investigations of the department. The investigation of the interesting magnetic properties of nanoscaled antiferromagnetic solids was continued in cooperation with the Zabel-group in Bochum. Using magnetic fingerprinting techniques, the dilute-antiferromagnet-in-a-field model was identified as the best description of the magnetic properties.

There is still a need to explore additional synthetic routes and create hitherto inaccessible compositions. For the solution based processes, non-oxide materials are especially interesting, and the synthesis of ordered mesoporous polymers and carbons – obtained after carbonization of such polymers – is explored in connection with the use of such high surface area polymers in biomass conversion processes. With respect to novel compositions, a range of mixed metal oxides of the spinel structure has been synthesized by adapted nanocasting processes. The compositions created include $Cu_{1.1}Mn_{1.9}O_4$, $CuCr_2O_4$, $CuCo_2O_4$, $NiCo_2O_4$ and $CoFe_2O_4$. These mixed metal oxides are interesting in catalysis for a number of reasons. They are highly active, noble metal free CO oxidation catalysts (the Cu-Mn-oxide resembles the well known Hopcalite catalyst), which partly are active already at room temperature. Moreover, the metal ions, especially the cobalt ions, are located in different coordination environments and are differently charged in the different compounds, and the analysis of these otherwise very similar materials gives important information on the active species in CO oxidation. An interesting synthetic method for the creation of ordered mesoporous oxides with novel framework composition was discovered in the alcohol-reduction of oxides with higher oxidation states. Thus, CoO could be synthesized by the reduction of Co_3O_4 with glycerol and other alcohols at temperatures around 300°C, similarly, Fe_3O_4 was obtained from Fe_2O_3. This process seems to be generic and can probably be extended to other oxides as well. Surprisingly, this reduction process was not only interesting with respect to the oxide. In looking at the reaction products which had formed from glycerol, it was discovered that allyl alcohol was produced with significant yields of up to 25%. The mechanism is unclear, yet, but probably involves a hydrogen transfer from either glycerol or a reaction intermediate.

A very exciting development with respect to the analysis of ordered mesoporous materials was the establishment of high resolution scanning electron microscopy (HR-SEM). The combination of the high structural quality of the materials synthesized and the unrivaled resolution of the Hitachi S-5500 microscope allowed the recording of images revealing unprecedented details of the surface structures of ordered mesoporous materials (Figure 1).

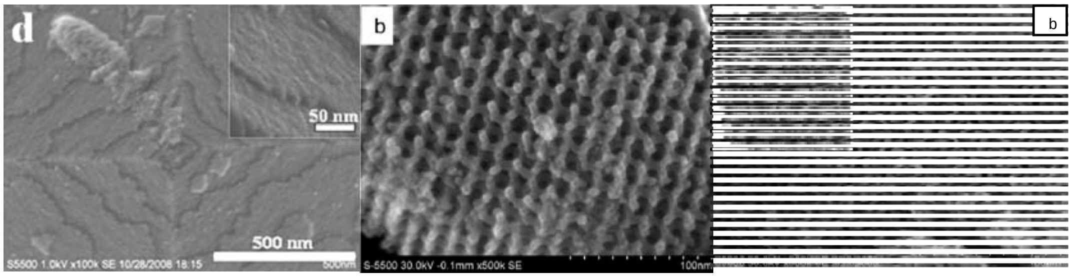

Fig. 1. HR-SEM images of different ordered mesostructured materials. Left: surface details of a FDU-16 crystal. The spherical micelles from which it grows are visible in the insert. Middle: nanocast Co_3O_4. Only one pore system of the parent KIT-6 is replicated. Right: ordered mesoporous silica KIT-6. Insert shows image simulation of a cut through the gyroid structure parallel to the 211 plane.

High surface area porous polymers have moved into the focus of the research of the department in the last years. This class of potential catalysts seems to be underexplored, primarily due to their low thermal stability. However, biomass conversion which is expected to increase in importance in the future, often proceeds at low temperatures in aqueous environment. Polymers seem to be highly suitable for application under such conditions. Therefore, a program to explore the synthesis and catalytic properties of such materials has been initiated and is meanwhile funded by an Advanced Grant of the ERC. Several pathways are explored for the synthesis of porous polymers. These include soft and hard templating approaches, sol-gel synthesis, and different types of phase separation processes. Several polymeric materials have already been prepared with high surface area and porosity. These include engineering polymers, such as polyetheretherketone (PEEK), which could be obtained with surface areas exceeding 100 m^2/g by a templating process with silica, which was leached after polymer infiltration, or poly-divinylbenzene which was polymerized in the pores of silica gel and could thus be produced with surface areas exceeding 500 m^2/g. Figure 2 shows a HR-SEM image of such a sample after removal of the silica with dilute NaOH solution. Also resorcinol-formaldehyde gels have been synthesized with surface areas of several hundred square meters per gram. While the latter material is mostly only used as a precursor for high surface area carbon, it has also been functionalized with acidic groups or noble metal particles for the production of catalysts based on the polymer.

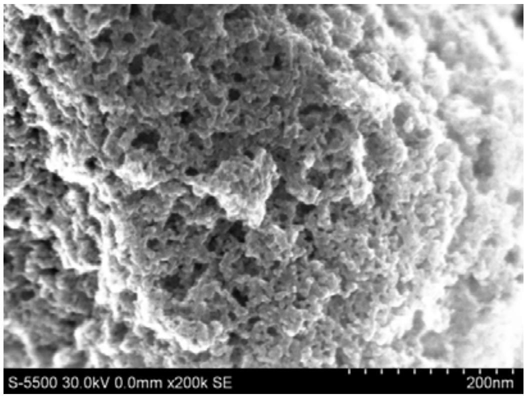

Fig. 2. HR-SEM image of a highly porous poly-divinylbenzene obtained by nanocasting from silica gel.

Such porous polymers are also the precursors for many kinds of porous carbon materials which are intensively studied in the department. An important prerequisite for the production of carbon is a high carbonization yield of the polymer, so that not all polymeric precursors are suitable for the synthesis of high surface area carbon. Very good precursors are condensation products of aromatic alcohols and formaldehyde, but also polyfurfuryl alcohol, as used in the synthesis of ordered carbons of the CMK-3 type, is often employed. Such ordered carbons were studied intensively, and in connection with the nanoengineering of catalysts, the surface functionalization of CMK-5 has been studied in depth. Using strategies, in which part of the pore system of CMK-

5 was blocked, selective functionalization of only one pore system was possible, which is an important step on the way to a carbon catalyst with different functionality selectively placed in each of the two pore systems of the CMK-5.

Carbon hollow spheres are interesting targets for different applications, such as matrix for electrode materials or as support for electrocatalysts. One approach for the synthesis of multilayer carbon vesicles relies on the use of aqueous emulsion synthesis starting from resol, tetraethoxysilane, Pluronics F127 and 1,3,5-trimethylbenzene as cosolvent. From such synthesis systems, multilayer polymer-silica vesicles in the size range of several 100 µm can be obtained. Calcination leads to the formation of carbon-silica vesicles, from which pure carbon multilayer vesicles can be prepared by leaching of the silica.

More interesting for applications, in which electronic conductivity is relevant, is a synthetic approach which results in the formation of graphitic hollow spheres. If 2,4-dihydroxybenzoic acid is polymerized with formaldehyde in the presence of lysine and the surfactant F127, a homogeneous spherical product is obtained. Suspending the initially solid polymer spheres in water for several hours leads to the formation of hollow polymer spheres, which can be carbonized to hollow spheres of amorphous carbon or, after introduction of iron species as graphitization catalyst, to graphitic carbon. These materials are presently being explored both as fuel cell catalysts and as matrix for the synthesis of iron phosphate electrode materials for Li ion batteries.

One problem for the highly porous carbon materials synthesized via organic sol-gel processes with subsequent carbonization is the complex synthetic procedure. The synthesis requires long reaction times and solvent exchange in order to retain the pore system of the initially formed organogel. In addition, while such materials are interesting catalyst supports, their properties as adsorbents are often inferior to many other carbon based materials due to the lack of microporosity. By careful fine-tuning of each synthesis step and an additional steam activation step it was possible to solve both problems. The overall preparation time could be shortened from more than two weeks to one day, and the activation step introduces a high fraction of micropores.

Fig. 3. Pilot-scale production of micro/meso-porous carbon aerogel. Here the production of the resorcinol-formaldehyde precursor gel is shown.

The resulting microporous carbon aerogel has excellent adsorption properties. Many of the undesirable components of cigarette smoke could be successfully removed under standard smoking conditions, and the new material outperformed standard coconut shell activated carbon by a wide margin. Due to these promising results the material was scaled-up to the 10 kg scale (Figure 3), and pilot tests are currently under way to explore the commercial potential of this promising material.

Publications resulting from this research area: 5, 9, 55, 56, 57, 58, 126, 127, 128, 129, 137, 148, 154, 162, 221, 282, 313, 314, 331, 352, 353, 395

External Funding: European Research Council Grant; IMPRS SURMAT; industry

Cooperations: C. Lehmann (Mülheim, DE); A.-H. Lu, W. C. Li (Dalian, CN); H. Zabel (Bochum, DE); Y. Wang, D. Y. Zhao (Shanghai, CN)

2.3.3 Research Area "Nanoengineered Catalysts" (F. Schüth / A.-H. Lu)

Involved: C. Baltes, M. Comotti, A. Dangwal Pandey, M. Feyen, C. Galeano, J. L. Galilea, R. Güttel, C. J. Jia, Y. Liu, Y. Meng, C. Neudeck, J.-J. Nitz, R. Palkovits, E. Passas-Lagos, M. Paul, K. Schlichte, M. Schwickardi, M. Soorholtz, G. Streukens, H. Tüysüz, G. H. Wang, S. S. Wang, C. Weidenthaler

Objective: The exciting developments in various fields, i.e. the controlled synthesis of metal or metal oxide nanoparticles, exact tailoring of porosity in many different porous solids, different templating and nanocasting concepts, together with unforeseen advances in electron microscopy, have made it possible to exactly tailor solid catalysts down to the nanometer scale. This means that particle sizes can exactly be predetermined, as well as the localization of different chemical functionalities. The success of these approaches is so substantial, that one can truly speak about "nanoengineering" of solid catalysts. This research field is so exciting and successful that it was one of the biggest groups of projects pursued in the department in the reporting period.

Results: Core-shell systems or yolk-shell systems (the core is located in a void which in turn is encapsulated by a shell) are very interesting, since such architectures can stabilize the core against sintering or corrosion. Such systems had already been introduced in the last report. At that time, a pathway for the generation of gold, encapsulated by a hollow zirconia shell, had been described, and the extremely high thermal stability of the composite had been proven: the system could be heated to 800°C without any sintering of the gold colloids in the core of the zirconia shells. This basis has now been extended into many different directions: the composition of the shell has been changed, as well as the size of the hollow spheres. Also the core materials have been modified, and the sizes of the gold cores in the zirconia shells can be adjusted. Some of the methods used will be highlighted here, more information can be found in the publications cited.

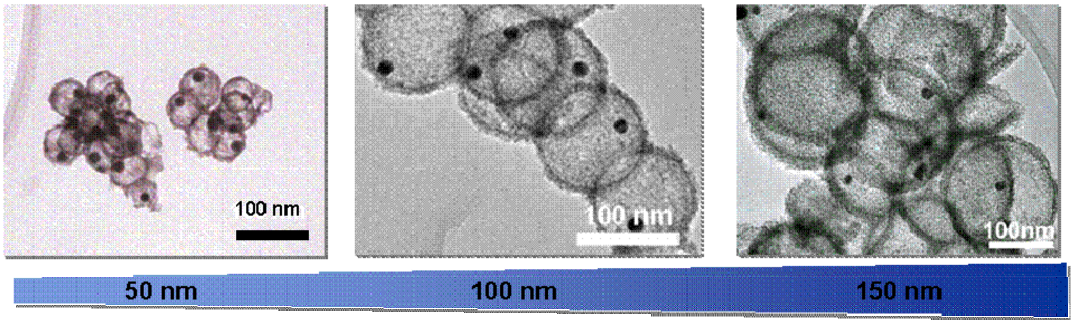

Fig. 1. Differently sized hollow zirconia spheres, each encapsulating a single gold particle. The size of the zirconia hollow spheres is determined by the amount of tetraethoxysilane which is used in the modified Stöber synthesis of the silica sacrificial template.

The modification of the size of the hollow spheres is relatively straightforward. The gold nanoparticles act – after proper functionalization with a surfactant – as the nucleation centers for silica in a modified Stöber process. After the growth of the silica spheres, the final coating with zirconia is applied, before the silica sacrificial template is leached. Due to this mechanism, the size of the silica spheres – and thus the resulting zirconia hollow spheres – can be tuned by the amount of tetraethoxysilane in the Stöber process. Figure 1 shows the range of sizes of the zirconia shells which is relatively easily accessible via this method.

Some shell materials can be synthesized by a similar method as the original zirconia shell (titania, ceria). However, other shells are less easily accessible, although they would be very interesting for the synthesis of catalytic materials. Carbon is an interesting catalyst and catalyst support, and thus a pathway was developed for the encapsulation of metal nanoparticles in hollow carbon shells. The route is slightly more complex: the pores in the zirconia coating of the previously described system are infiltrated with a carbonizable polymer before dissolution of the silica sacrificial template. After carbonization, both the silica and the zirconia are dissolved, resulting in a metal particle in a carbon shell. In the course of this development, it was found that a porous silica shell on the impervious silica template is even more suitable for the formation of the porous carbon (Figure 2).

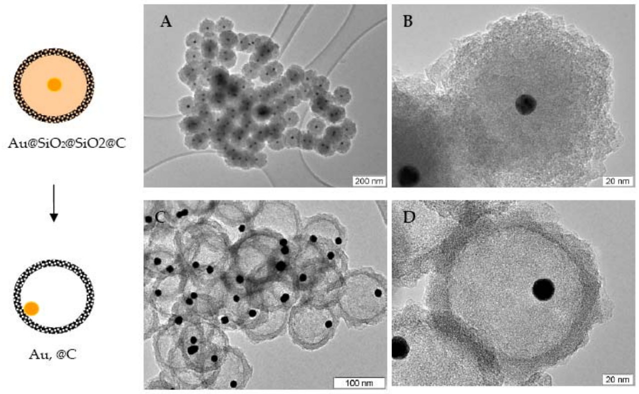

Fig. 2. Carbon encapsulated gold nanoparticles. The synthesis starts with gold particles which are coated with an impervious silica sphere, then with a porous silica shell. The pores in this shell are filled with a polymer which is carbonized (top). After leaching of the silica, the final product (bottom) is obtained.

In numerous experiments it has been established that the 15 nm sized gold cores produced by the Turkevich method are ideal for the encapsulation. However, smaller gold particles are more interesting for catalytic applications, as also shown in many experiments, both by our group and by others. Decreasing the size of the gold cores was therefore an attractive target. It was found that under certain conditions the silica shells are not fully impervious, but that the gold can be leached out. Aqua regia is suitable for this leaching process, and the gold can be fully removed, leaving a 15 nm sized void in the center of the silica spheres (which can, incidentally, be filled with another metal).

However, partial leaching results in complete loss of activity for CO oxidation, due to the chlorine which acts as a catalyst poison. Thus, gold was leached with cyanide solution. Here the concentration can be adjusted according to the stoichiometry of the reaction so that target gold sizes could be achieved. Using this pathway, gold particle sizes between 5 and 15 nm were accessible, and in CO oxidation it could be shown that in this particle size range the catalytic activity is independent of particle size, i.e. the TOF does not change. On the other hand, it was shown that titania doping of the gold cores led to a strong increase in catalytic activity. Catalysts in which 15 nm sized gold particles were modified with small amounts of titania had catalytic activities which typically are observed only for highly active catalysts with gold particles in the size range below 5 nm. This demonstrates the strongly modifying effect which the support has on the activity of gold catalysts. A non-interacting support, such as the carbon described above, incidentally leads to catalytic activities which are much lower than the activities of the zirconia encapsulated gold particles.

The question of the support effect on the catalytic activities of small gold particles has been intensively studied in the reporting period. Since these gold particles are deposited by the colloidal deposition method, a high degree of control is exerted over the formation of the gold particles. Many different novel support materials have been studied, and with MgO and $Mg(OH)_2$ as support, the most active catalysts so far reported have been synthesized. At a space velocity of 80,000 ml $g^{-1}h^{-1}$, full conversion was reached even at temperatures as low as –90°C. The activity is very dependent on the moisture present in the system, as had been reported before for other catalysts as well. However, this high activity is lost at temperature around 0°C, before full conversion is again reached at 180°C. This behavior is attributed to the presence of an active oxygen species at low temperature, which, however, is desorbed upon heating, overcompensating the rate increase of the surface reaction, and thus leading to the negative apparent activation energy.

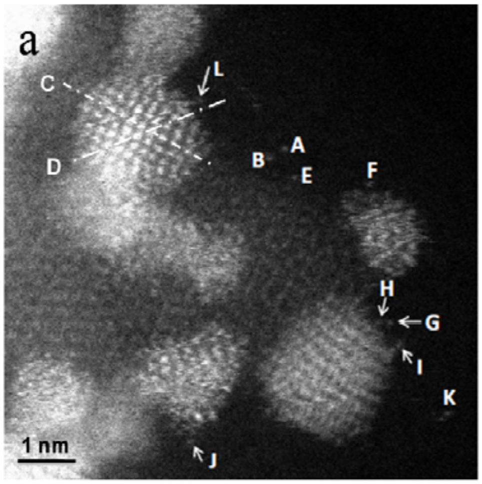

Fig. 3. HAADF-STEM images of colloidally deposited gold particles on iron oxide. The labelled atoms are single gold atoms produced in the TEM analysis and can be used for intensity calibration. Along the lines, the particles are up to 3-4 layers thick.

In the literature, it had been suggested that highly active catalysts based on iron oxide require the presence of bilayer, sub-nm sized gold species. Since the colloidal deposition method should exclude the formation of such small gold species, catalysts were synthesized by this method for comparison. These catalysts were found to have similar activities – based on catalyst mass – as the catalysts which had the bilayer gold structure. The colloidally deposited catalysts were extensively characterized by HAADF-STEM, and the presence of small gold clusters could be excluded. Gold particles were typically four-layer particles, as proven by simulation of the electron microscopy images.

It was also shown in the reporting period that the presence of gold is not necessary for high activity CO-oxidation catalysts. Nanocasted and highly porous Co_3O_4 was found to be as active as gold-based catalysts, and if the cobalt oxide was additionally modified with silica, the activity was even higher. By now, a number of other – typically spinel-type – mesoporous catalysts with high CO oxidation activity has been identified. By synthesizing different, specifically tailored spinel-type oxides with cobalt selectively placed on tetrahedral or octahedral sites, it could be shown that both Co^{2+} and Co^{3+} can lead to high catalytic activity, in contrast to reports in the literature.

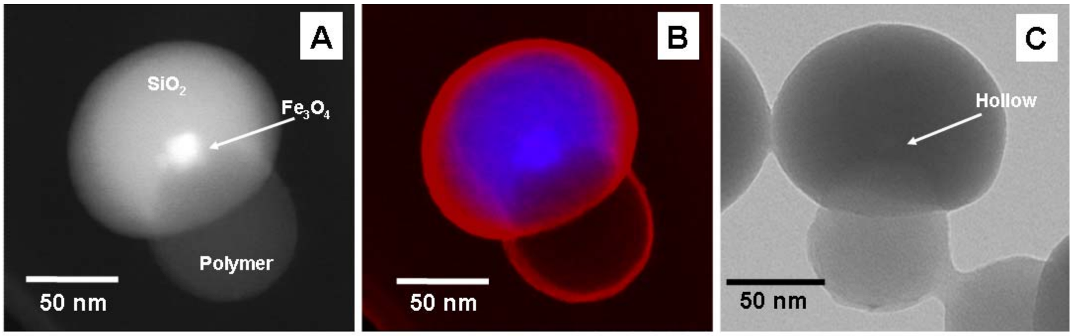

Fig. 4. (a) Dark field STEM image of the mushroom structure, obtained by growth of poly(styrene-co-divinylbenzene) on iron oxide, followed by a second growth of silica. (b) Overlay of SEM and dark-field STEM of the same structure. (c) STEM image of same material after HCl leaching, the iron oxide particles are dissolved and a corresponding void is left.

Core-shell catalysts can also be produced starting from oxide cores. If iron oxides are used, the resulting material can have superparamagnetic or ferromagnetic properties, depending on the size and exact composition of the cores. Growth of specific shells can be induced by similar methods as for the gold cores. For each system, however, specific conditions have to be established. Iron oxides can ideally be coated with polymer, for instance, poly(styrene-co-divinylbenzene). The divinylbenzene moiety of the copolymer provides the crosslinking and thus mechanical stability. Based on this composite – an iron oxide core and the polymer shell – further functionalized solids can be produced. Sulfonation of the polymer creates acidic sites, and the resulting material is an acidic catalyst which can be recycled after magnetic separation. More complex composites can be created after an additional coating of the iron oxide/polymer core-shell system with an additional layer of silica. If the iron oxide core is not covered completely with the polymer, the silica nucleates on the iron oxide still exposed, resulting in the formation of “mushroom” structures. These can be further modified, for instance, by carbonization of the polymer part or by selective leaching of the iron oxide cores.

Iron oxides can also be encapsulated in the pores of ordered mesoporous materials. In order to check what degree of control can be achieved with respect to localization of particles in such pore systems, an iron oxide/CMK-5 material has been synthesized with the iron oxide exclusively deposited in the inside of the carbon tubes (Figure 5). This system, incidentally, turned out to be an excellent catalyst for ammonia decomposition. For the selective deposition of iron oxide in the tubes, first the inside of the pores of SBA-15 was coated with polyfurfurylalcohol which was then pyrolized to result in formation of a carbon coating. The pores in the silica-carbon composite were filled with iron nitrate solution and heated to 1000°C, resulting in the formation of γ-Fe_2O_3 particles inside the carbon tubes. Leaching with dilute NaOH removed the silica and opened up an additional pore system. Detailed XRD analysis of this system and other iron-based catalysts ex-situ and in-situ revealed that under reaction conditions iron nitride phases are formed, the exact composition of which depends on the reaction conditions.

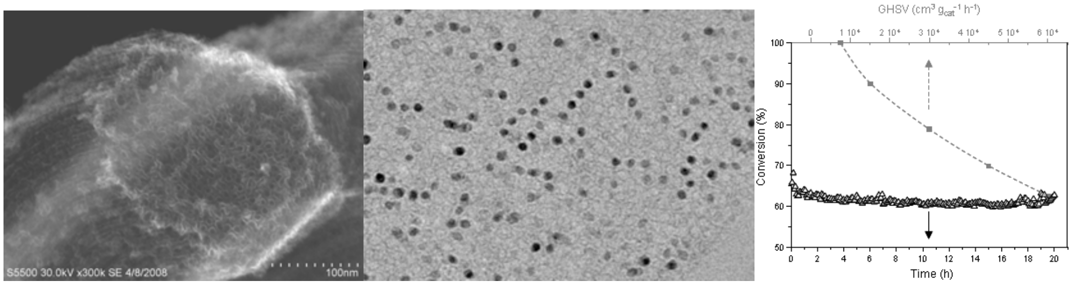

Fig. 5. Left: HR-SEM of CMK-5, the pore openings of the carbon tubes with 6 nm internal diameter can clearly be seen. Middle: TEM of microtomed γ-Fe_2O_3/CMK-5, the sample was cut perpendicular to the channel axes. Left: Performance of the system in decomposition of pure ammonia. Such catalysts have very high stability and excellent activity.

Based on a high surface area carbon material, another highly interesting catalyst system was fabricated. In the group of Markus Antonietti it had been discovered that pyrolysis of dicyanopyridine under certain conditions results in the formation of a high surface area carbon-nitrogen material. The idealized structure of this material contains fragments which resemble the bipyrimidyl-motif of the ligands in the molecular Periana catalyst for methane oxidation with sulfur trioxide in oleum to methylbisulfate. This triggered the idea of constructing a solid analogon of the Periana-system. Various pathways for introducing platinum into the C-N-material were explored, but it was found that already simple impregnation led to strong binding of platinum to the solid (Figure 6). Different analytical methods revealed that the platinum is most probably atomically dispersed in the solid and that most binding sites are occupied with platinum centers. The activity of the resulting solid per platinum site is in the same range as for the molecular counterpart, but the solid catalyst can be recycled without loss in activity.

Publications resulting from this research area: 46, 146, 203, 223, 224, 226, 263, 264, 272, 274, 277, 302, 306, 307, 308, 316, 330, 332, 345, 351, 354, 369, 373, 427

External Funding: Deutsche Forschungsgemeinschaft (SFB 558); Leibniz award; industry

Cooperations: M. Antonietti (Golm, DE); C. Christensen (Lyngby, DK); M. Muhler (Bochum, DE); O. Terasaki (Stockholm, SE); R. Schlögl (Berlin, DE); C. W. Lehmann, R. Palkovits, W. Schmidt, (Mülheim/Ruhr, DE)

2.3.4 Research Area “Hydrides for Hydrogen and Energy Storage” (F. Schüth)

Involved: J. Döring, M. Felderhoff, S. Grabbe, K. Hauschild, R. Pawelke, K. Peinecke, A. Pommerin, W. Schmidt, H. Y. Shao, N. Spielkamp, G. Streukens, C. Weidenthaler, B. Zibrowius

Objective: Hydrides, especially complex light metal hydrides, are intensively studied, both for their attractive properties as potential hydrogen storage materials and for fundamental reasons, since relatively little is known about many of these seemingly simple materials. In the past, the work had been primarily concentrated on doped $NaAlH_4$ as storage material, in cooperation with Opel. However, the stoichiometry does not allow reaching the target storage densities with this material. The scope of the work has therefore been broadened substantially, in order to explore the chemistry of complex hydrides more widely, to further develop synthesis methods – most notably mechanochemical methods, such as ball-milling – , and to study the suitability of different hydride systems also as heat storage materials.

Results: One-step synthesis of complex hydrides by ball-milling methods was in the center of the attention during the last reporting period. While some studies were still carried out on the $NaAlH_4$ system for use in miniaturized fuel cells and for scale-up, work has been expanded to other hydrides, especially to rare earth aluminum hydrides. Also methodical developments were pursued: ball milling is the most often used method for the synthesis of hydrides. However, under the conditions of ball milling, unstable hydrides decompose almost invariably, due to the high energy transferred. This has severely hampered the synthesis of novel, unstable hydrides up to now. Since many hydrides, which are unstable at room temperature, are thermodynamically stable at lower temperatures, cryo-milling was developed for the synthesis of such materials. Thus, different alanates (Li, Na, K) could directly be synthesized from the corresponding binary metal hydride and alane (Figure 1). At room temperature, milling of AlH_3 leads to rapid decomposition to aluminum metal and hydrogen. This method is now being explored for the synthesis of other complex hydrides. Ball milling is also highly suitable for the synthesis of other compounds. $NaAlD_4$, required for neutron diffraction studies, is not easily synthesized by conventional methods. Ball milling, on the other hand, allows easy access to this compound according to equation (1):

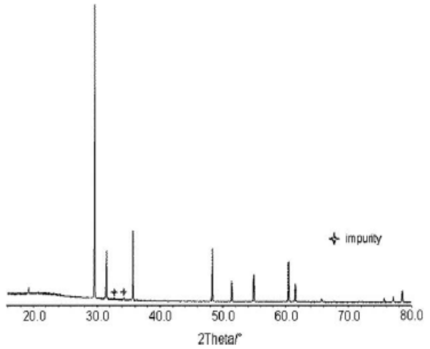

Fig. 1. X-ray diffraction pattern of $NaAlH_4$, synthesized at –196°C from NaH and AlH_3.

$$LiAlD_4 + NaF \rightarrow NaAlD_4 + LiF \qquad (1)$$

The corresponding potassium compound can also be synthesized following this route, but surprisingly, $Ca(AlD_4)_2$ and $Mg(AlD_4)_2$ did not form, although thermodynamically possible. Ball milling was also explored for the synthesis of other compounds, such as in the preparation of ternary potassium transition metal halides. Several halides, some of which hitherto not reported, could by produced in a very simple manner.

The extension of the ball milling technique had originally started with the doping of $NaAlH_4$ with titanium as decomposition catalyst. It was also used for the doping with other catalysts, such as cerium or scandium, which are among the most effective catalysts for the dehydrogenation/hydrogenation reaction.

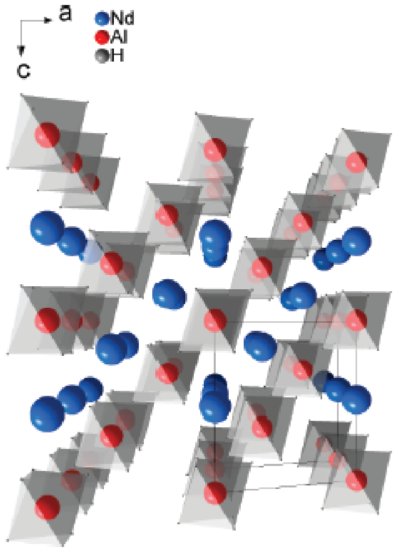

Fig. 2. Crystal structure of $NdAlH_6$ in projection along [010]. Hydrogen positions were not refined.

Especially the cerium doped system was found to be promising, since the resulting material has fast kinetics as well as stable cycling properties. The successful doping reaction with rare earth compounds initiated attempts at the synthesis of the pure rare earth aluminum hydrides. These were successful for RE = La, Ce, Pr, and Nd. In a metathesis reaction of the rare earth chlorides $RECl_3$ with $NaAlH_4$, isostructural solids were obtained for all rare earth compounds, judging from the XRD patterns. However, structure solution directly from the powder patterns proved to be difficult. Nevertheless, after quantum chemical structure calculations, the powder patterns could be refined and plausible structures could be suggested (Figure 2). The hydrogen content of the materials is too low for technical applications. Nevertheless, it is remarkable that a new structural motif in aluminum hydrides could still be discovered in spite of the tremendous amount of work invested in this field.

After several years of basic research in the field of complex sodium aluminum hydride, the focus is presently on small demonstration projects. In cooperation with ZBT and IUTA the integration of a $NaAlH_4$ storage tank into the thermal loop of a HT-PEM cell was shown for the first time. This is now extended to the usage of complex metal hydride systems for the decoupling of heat and electricity generation with PEM fuel cells for single family houses.

Since the storage capacities of all the aluminum hydrides studied so far fall short of the requirements of the automotive industry, also other hydrides were included in the study.

One of the more promising materials – and long studied in the institute by B. Bogdanović since the 1980s – is MgH_2. This can be obtained in nanostructured form, if it is first reacted with anthracene and then with catalytic amounts of $TiCl_4$. Subsequent hydrogenation then leads to the formation of the final nanostructured and titanium-catalyzed MgH_2. The hydrogen release for this nanostructured and titanium-containing MgH_2 occurs at temperatures more than 100°C lower than for the bulk material. Whether this is due to the nanostructuring, the titanium, or both is unclear, yet.

The original target application for MgH_2 was heat storage. The hydrogenation/ dehydrogenation reaction is associated with an enthalpy change of 0.9 $kWh\ kg^{-1}$, rather high compared to other materials. Since the temperature range in which MgH_2 operates corresponds closely to the range relevant to concentrating solar thermal power plants, work has been initiated to explore the use of metal hydrides in such power plants.

Complex hydrides as catalysts for hydrogenation reactions of unsaturated bonds in organic molecules have also intensively been studied. However, while in the liquid phase such reactions were successful, as shown for the case of stilbene, gas-phase reactions proved to be very difficult. The hydrogenation of 1,3-butadiene was studied as test reaction, and while the complex hydrides were moderately active, no remarkable selectivities were observed, and reproducibility problems associated with a very sensitive catalyst slowed down progress. Due to the unimpressive catalytic properties and the problems described, this line of research was eventually terminated.

Publications resulting from this research area: 11, 25, 80, 81, 159, 160, 172, 175, 229, 263, 276, 379, 380

External Funding: GM/Opel; AIF; BMBF; Energieforschung NRW

Cooperations: A. Heinzel, S. Peil, J. Wartmann (Duisburg, DE); M. Fichtner (Karlsruhe, DE); M. Dornheim (Geesthacht, DE); C. Wolverton (Evanston, USA)

2.3.5 Research Area “Nanostructured Optical Materials” (F. Marlow)

Involved: R. Brinkmann, D. Schunk, C. Mendive, Muldarisnur, I. Popa, P. Sharifi

Objective: Nanostructures with length scales in the order of the wavelength of light have specific effects on electromagnetic fields. Photonic crystals are highly ordered versions of them. Synthesis, modification, and characterization of such materials are investigated in this research area in order to develop novel functional materials.

Results: The self-assembly of well-ordered macroporous materials, especially of artificial opals, was investigated in this research area. This method is one basic approach to photonic crystals which are potential key materials for future optical technologies. The refinement and understanding of one of the currently known opal fabrication methods was the focus of the research.

As reported in a former report we have developed a new efficient technique for opal fabrication. This method exploits capillary forces and is much easier to handle than the known methods. Our method delivers large-area, homogeneous opal layers with a controlled crack structure. The cracks are typical defects for all kinds of artificial opal layers. Besides the cracks, also the opal lattice turned out to be strongly aligned in opals fabricated by our method (Figure 1). This is considered as an important step to mono-crystalline opals which are, up to now, not existing. The current opal films can be understood as intergrowth structures of two different fcc lattices.

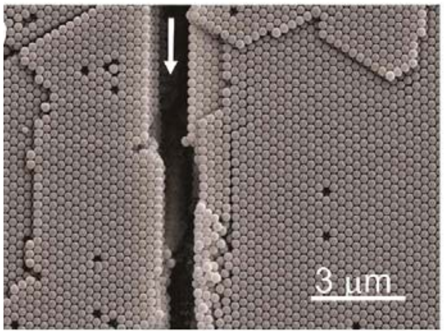

Fig. 1. SEM picture of an opal fabricated by the capillary deposition method (CDM). The white arrow is the growth direction.

The detailed understanding of the opal self-assembly process is another topic of our research. The opal formation is divided into two temporal phases: the wet assembly and the drying. Both are of relevance for the quality of the opals. We have followed the second phase in-situ by optical spectroscopy and found slow rearrangement processes during and after water removal. It takes some hours till the final nanosphere arrangement is formed.

To improve our knowledge on the lattice disturbances we have performed neutron scattering experiments at the GKSS Geestacht. Our results deliver a further strong indication that the opal films fabricated by CDM consist of an intergrowth structure of two lattices only. Rocking curves have shown long-range lattice deformations described by a mosaic model. Theses deformations of less than 3° in the lattice directions have been quantified for the first time.

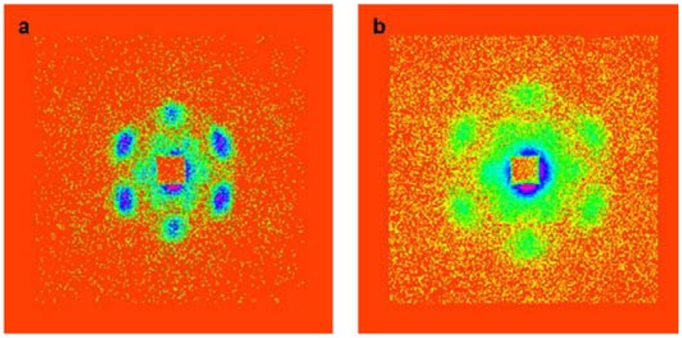

Fig. 2. Diffraction pattern for an opal film made by 264 nm polystyrene spheres (a) and for a TiO_2 inverse opal film (b) fabricated from a template as in Fig. 1a. The position of the peaks delivers lattice constants of 360 and 269 nm, respectively.

Inverse opals fabricated by a sol-gel technique turned out to feature much stronger deformations. The crystal parts fluctuate by about 11° against the mean lattice orientation. These deformations exclude a number of applications of these special photonic crystals such as the use of slow photon effects. Therefore, the search for self-assembled photonic crystals different from traditional artificial opals (other inorganic materials) and avoiding inversion steps have been started.

Publications resulting from this research area: 53, 82, 120, 194, 208, 212

External funding: International Max Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat); Nano Energy Technology Center (NETZ)

Cooperations: H. Zabel (Bochum, DE); H. Eckerlebe (Geestacht, DE); H. Wiggers / C. Schulz (Duisburg, DE); E. Mazur (Harvard, USA); T. Voss (Bremen, DE); M. Tiemann (Gießen, DE); M. Rohwerder (Düsseldorf, DE)

2.3.6 Research Area "Solid Catalysts and Reaction Systems for Utilization of Cellulose and Sugars" (R. Palkovits)

Involved: A. Ruppert, K. Tajvidi, S. Zhou, K. Pupovac, M. Kükrek, M. Mischner, W. Hofstadt

Objective: Lignocellulose presents a potential future carbon source for production of fuels and chemicals. The high density of functional groups opens numerous possibilities for tailored chemical transformations to novel target molecules. With regard to catalysis, however, this over-functionalization makes high demands on catalyst and process development. Today's refineries are based on gas phase processes at high temperatures introducing functionality into non-polar feedstocks. In contrast, transformations based on lignocellulose require liquid phase processes in polar solvents at rather low temperatures. Several projects were designed to tackle these challenges focusing on the development of suitable solid catalysts and reaction systems for the efficient utilization of cellulose, sugars and polyols.

Results: One of the major challenges with regard to the development of catalysts and processes for the efficient transformation of cellulose refers to the fact that cellulose is hardly soluble in any conventional solvent complicating utilization of solid catalysts. Ionic liquids, especially based on alkyl imidazolium salts, dissolve cellulose on a molecular level. Consequently, various attempts have been made to hydrolyse cellulose to glucose or 5-hydroxymethylfurfural (5-HMF) in ionic liquids applying mineral and organic acids or metal salts. However, separation of such reaction products from polar ionic liquids is challenging because glucose and 5-HMF are difficult to extract and not thermally stable. An alternative is the depolymerization of cellulose to cello-oligomers in ionic liquids catalyzed by acidic ion exchange resins or via slow addition of conventional molecular acids. Therein, the slow release of protons into the reaction solution renders a controlled depolymerization to cello-oligomers of narrow degree of polymerization possible. Such cello-oligomers can be precipitated by simple addition of water and show a significantly accelerated enzymatic hydrolysis to glucose.

Concerning the direct transformation of cellulose or sugars into potential platform molecules, not only separation of such products from ionic liquids, but also selectivity to certain target molecules becomes an issue. In addition to hydrolysis of cellulose to glucose and further dehydration to 5-HMF, re-hydration to levulinic acid or formation of humins via polymerization reactions occur. Reactive extraction presents an approach to address both issues separation and selectivity. Therefore, two-phase systems were designed based on dehydration of fructose or glucose to 5-HMF in a polar solvent, including water or the acidic ionic liquid 1-H-4-methylimidazolium chloride [MIM]Cl, and continuous extraction of 5-HMF in an organic layer with subsequent conversion into products of lower polarity (Figure 1). In a first step, the individual reactions have been investigated. Concerning the polar phase, dehydration is carried out either in pure [MIM]Cl serving as both solvent and acid catalyst or in aqueous phase adding a suitable solid acid. With regard to dehydration in [MIM]Cl, water management is essential. Without water removal, 5-HMF yields remain low, while reduced pressure enforces formation of humins. In contrast, a simple air stream through the solution results in full conversion and 95% selectivity for 5-HMF after 5 h at 90°C. With regard to efficient dehydration in aqueous phase, temperatures above 140°C and solid acids with appropriate concentration and strength of acid sites are required. Especially, surface functionalized silica and carbon materials showed promising results and further attempts will be made to identify correlations between the properties of the materials and their activity in sugar dehydration. Suitable transformations with regard to the organic layer include oxidation to furan-2,5-dialdehyde (A), a potential monomer for polymer production, hydrogenolysis to 2,5-dimethylfuran or 2,5-dimethyltetrahydrofuran (B), which are discussed as biofuels, or aldol condensation with suitable aldehydes (C), e.g. acetone, towards synthesis of chemical building blocks. The extracting solvent has not only to allow proper phase separation with the polar phase and sufficient solubility of 5-HMF, but also to be suitable for the attempted further conversion. Current investigations focus not only on the design of reaction systems, but also on the development of suitable catalysts, including solid acid and solid base materials for such coupled reactions. Therein, first studies of combined reaction systems emphasized that sugar

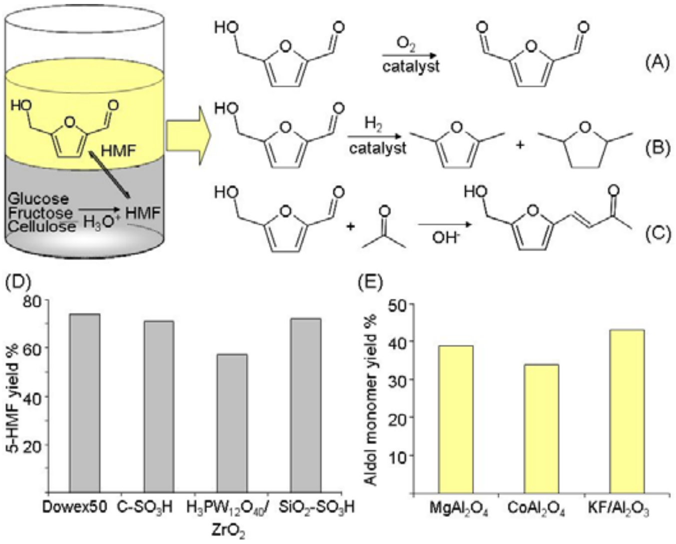

Fig. 1. (A-C) Possible two-phase systems combining dehydration of sugars to 5-HMF, extraction and subsequent conversion to products of lower polarity; (D) dehydration of fructose in aqueous phase in the presence of an extracting phase; (E) aldol condensation of 5-HMF with acetone.

dehydration and reactive extraction depend on a proper balance between extraction of 5-HMF and subsequent transformation. Consequently, extraction and reaction kinetics have to be investigated.

An alternative strategy relates to the direct transformation of cellulose via combined hydrolysis and hydrogenation in aqueous phase yielding sugar alcohols which are stable against further degradation. In a first approach, mineral acids (H_3PO_4 and H_2SO_4) and supported noble metals (Pd, Pt and Ru on activated carbon) were studied to develop a quantitative composition-activity relationship model (Figure 2). The noble metal had a strong impact on product selectivity, while acid strength and concentration determined the conversion, indicating a two-step process via hydrolysis of cellulose to yield glucose, which undergoes further hydrogenation and hydrogenolysis. Combining H_2SO_4 and Ru/C, 60% yield of sugar alcohols could be reached. Furthermore, optimization of the ruthenium catalysts with respect to particle size showed a strong effect and the influence of support material and particle size on product selectivity has to be investigated (Figure 3). Further investigation revealed that among various acids, heteropoly acids (HPA) in

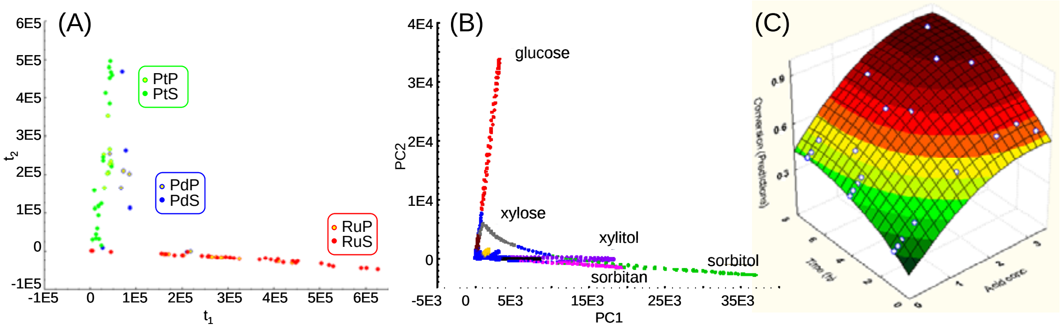

Fig. 2. (A) Score plots t_1/t_2 showing an overview of the 85 observation contained in the primary data set (catalysts choice is indicated with Pt, Pd, Ru and the used mineral acid with P or S, respectively. (B) Loading plot p_1/p_2 of the products formed in celullose hydrogenolysis. (C) Composition-activity model of the Ru/C – H_2SO_4 system (SVM plot) based on the dataset.

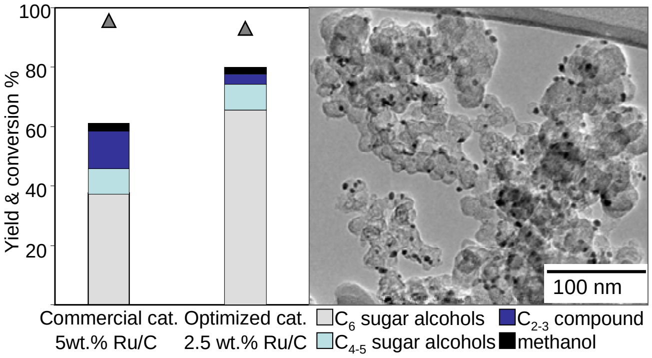

Fig. 3. Activity of commercial 5 wt.% and optimized 2.5 wt.% Ru/C catalysts (TEM) combined with 2.5 wt.% H_2SO_4 in the hydrogenolysis of cellulose (500 mg cellulose, 100 mg Ru/C, 10 ml H_2SO_4, 3 h, 160°C, 50 bar H_2 at 25°C).

combination with supported Ru catalysts (Ru/C) allow not only for excellent conversion of cellulose with > 80% yield of C_4 to C_6 sugar alcohols and 91% carbon efficiency at only 160°C, but may even be applied effectively in the transformation of spruce as real biomass feedstock (Figure 4). Crucial points refer to synthesis of suitable solid acids and bifunctional catalysts combining acid and hydrogenation function. Therein, factors influencing conversion and selectivity have to be identified. Based on ion exchanged HPAs and surface functionalized polymer or silica materials, first promising systems could be prepared. Future investigations will not only cover further catalyst development and optimization, but also concentrate on kinetic and mechanistic studies to gain insights into the complex reaction network and factors influencing selectivity to certain target products.

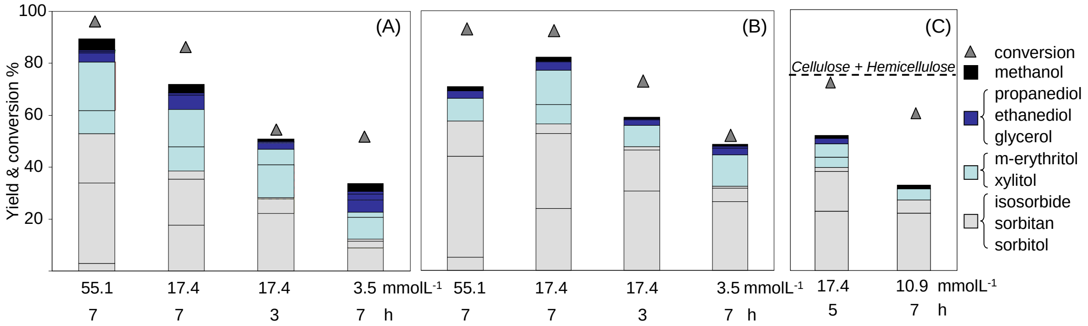

Fig. 4. Activity of (A) $H_4SiW_{12}O_{40}$ and (B) $H_3PW_{12}O_{40}$ combined with Ru/C in the conversion of cellulose to sugar alcohols and application of (C) $H_4SiW_{12}O_{40}$ and Ru/C in the transformation of spruce (10 ml H_2O, 100 mg Ru/C, 160°C, 50 bar H_2 at 25°C).

Publications resulting from this research area: 79, 97, 98, 99, 225, 368, 370, 371, 372, 391, 408

External funding: Cluster of Excellence “Tailor made fuels from biomass” RWTH Aachen; Robert-Bosch Foundation; Nano Energy Technology Center (NETZ); Fonds der Chemischen Industrie

Cooperations: J. Procelewska, R. Rinaldi, F. Schüth (Mülheim/Ruhr, DE); W. Leitner / N. Theyssen (Aachen / Mülheim/Ruhr, DE)

2.3.7 Research Area "Depolymerization of Cellulose in Ionic Liquids"

(R. Rinaldi / F. Schüth)

Involved: N. Meine, J. vom Stein

Objective: Depolymerization of cellulose is desirable to produce cello-oligomers or glucose, which can be used as entry-point into biorefinery schemes for the production of chemicals and biofuels. Nevertheless, the recalcitrance of the biopolymer poses serious challenges to the chemical and biological processing of cellulose. The solubilization of cellulose in ionic liquids (ILs) completely disassembles the supramolecular structure of the cellulosic fibers. This markedly improves the reactivity of cellulose and enables the depolymerization of cellulose under mild conditions. In this group of projects, we are developing new strategies to circumvent the recalcitrance of cellulose using ILs.

Results: The addition of acid species into a solution of cellulose in 1-butyl-3-methylimidazolium chloride (BMIMCl) initiates a complex reaction chain. In the first step, cellulose undergoes depolymerization through hydrolysis of 1,4-*β*-glycosidic bonds. Either smaller 1,4-*β*-glucans (cello-oligomers) or glucose can be formed at this stage. In the presence of acidic species, glucose is likely to be dehydrated, producing a number of compounds, such as 5-hydroxymethyl-furfural (5-HMF), levulinic acid, formic acid, and several others. These products are prone to recombination with sugars or oligosaccharides via aldol condensation, resulting in polymers with undefined structures and stoichiometry called humins. In practice, stopping the process at the cellooligomer stage is crucial because they can be easily isolated from the ILs upon addition of water (cf. Figure 1), while the workup for the extraction of

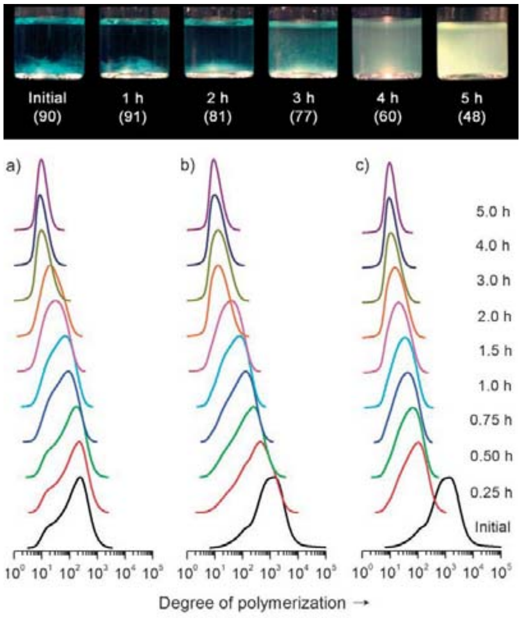

Fig. 1. (*top*) Hydrolysis of microcrystalline cellulose. Appearance of cellulose recovered from BMIMCl by addition of water after the reaction times indicated. The values between parentheses represent the percentage of isolated cellulose. (*bottom*) Distribution of apparent degree of polymerization of celluloses isolated from BMIMCl solution during the reaction: a) Microcrystalline cellulose (Amberlyst 15DRY). b) α-Cellulose (Amberlyst 15 DRY). c) α-Cellulose (*p*-TSA).

sugar and dehydration products is normally very difficult, or not even achievable, due to the high solubility of the products in both ILs and water.

A novel strategy for controlling the depolymerization of cellulose in ionic liquids has been the use of solid acids as source of H_3O^+ species for the reaction. Performing the acid-catalyzed depolymerization of cellulose using Amberlyst 15DRY enables the control of the reaction progress effectively. As a result, cello-oligomers with a tunable degree of polymerization can be conveniently produced (cf. Figure 1). The acidic resin releases H_3O^+ species into the solution, controlling the initial rate of depolymerization. The preferential cleavage of large polymeric molecules occurs because of statistical reasons. The preference can be understood considering that cello-oligomers are produced upon cleaving the polymeric chain at any position, while formation of glucose requires specific cleavage at the ends of cellulose. In this manner, the formation of glucose is not favored at the beginning of the depolymerization process, because the reaction mixture contains large polymeric chains at this reaction stage. Therefore, the high selectivity for cello-oligomers is a feature linked to cellulose rather than to the acid catalyst used. A high degree of control of the depolymerization reaction can be achieved also in the case of molecular acids, if they are added slowly over time to the reaction batch, thus mimicking the slow ion exchange process occurring over the solid acids.

Almost quantitative conversion of cellulose into fermentable sugars is achieved when starting from the cello-oligomers. Figure 2 shows the performance of a commercial cellulase preparation (Celluclast®, *T. reseei*) in the enzymatic hydrolysis of several cellulosic materials. In contrast to untreated α-cellulose and to cellulose regenerated from ILs, which show substrate conversions of 46 and 79%, respectively, the cello-oligomers are nearly quantitatively hydrolyzed (94%) by cellulases within 4 h at 45°C. Furthermore, this reaction produces exclusively cellobiose and glucose, *i.e.* the enzymatic selectivity is maintained. The ratio between cellobiose and glucose, however, depends heavily on the pretreatment of cellulose and on the substrate conversion.

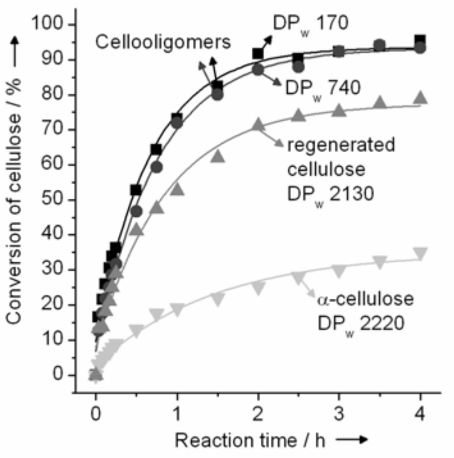

Fig. 2. Enzymatic hydrolysis of α-cellulose, cellulose regenerated from IL and cellooligomers. Conditions: substrate (eq. 1 g of dry cellulose), cellulase (Celluclast®, 350 U/g substrate), pH 4.5 (acetate buffer), 45°C.

Surprisingly, no marked effect of the degree of polymerization on the enzymatic performance is observed in the reactions carried out with cello-oligomers smaller than 800 anhydroglucose units (AGU). This finding has important implications for process development. Starting from native cellulose (DP 2,000 - 10,000 AGU), suitable cellooligomers for the enzymatic hydrolysis would be already produced after 3 to 16 scissions in the cellulosic chains, which is reached in less than 1 h through the acid-catalyzed depolymerization in IL. Owing to the preference for the production of cellooligomers over the formation of glucose in the earlier stages of acid-catalyzed depolymerization, losses of glucose, due to its dehydration, are completely suppressed. Consequently, the integration of acid- and enzyme-catalyzed conversion unites the advantages of both “worlds”, bringing rapid and quantitative conversion of cellulose to fermentable sugars.

In summary, the findings presented here demonstrate that a fast, efficient and integrated process for the complete hydrolysis of cellulose to fermentable sugars is indeed feasible. On a laboratory scale, the acid-catalyzed depolymerization of cellulose achieved nearly quantitative yield of cellooligomers (95-100%) within 0.5 to 1 h. Likewise, commercial cellulase preparations hydrolyze the cellooligomers to a mixture of glucose (40%, 4 h) and cellobiose (54%, 4 h), reaching a conversion of 94% in 4 h. These results are remarkable, since the overall process is accelerated by about one order of magnitude at much higher yields of fermentable sugars. For the sake of comparison, for sugar yields exceeding 50%, pretreatment of cellulose by conventional means is required that then leads to reaction times of days in enzymatic hydrolysis. Finally, research on the further optimization of the cellulase “cocktail” is required to take full advantage of the high accessibility of cellulosic chains in the cellooligomer hydrogel. This is an important issue for future research, because cellulases account for ca. 40% of the cost of cellulosic ethanol.

Publications resulting from this research area: 97, 98, 99, 244, 245, 328, 359, 360, 390, 391

External funding: Cluster of excellence Tailor-made fuels from biomass (RWTH Aachen)

Cooperations: J. Büchs, A. Spiess (Aachen, DE); R. Palkovits, W. Thiel (Mülheim/Ruhr, DE); W. Leitner / N. Theyssen (Aachen / Mülheim/Ruhr, DE)

2.3.8 Research Area “Exploration of Nanoporous Solids” (W. Schmidt)

Involved: U. Wilczok, A. Cepak, C. C. Pavel, H. Bongard, J. Nitz, B. Spliethoff

Objective: Nanoporous solids possess pores with sizes equivalent to molecular dimensions and serve as molecular sieves and selective catalysts in various applications. Pore diameters as well as pore shapes and pore organization determine the interaction with molecules from fluid phases. Further crucial factors are crystallite sizes and morphologies. These parameters determine adsorptive and diffusional properties as well as catalytic activity of these solids. Tailoring of textural and/or surface properties of particles allows subtle modifications with respect to pore accessibility, diffusivity of guest molecules, and solid-fluid interaction. Preparation and detailed characterization of nanoporous solids is subject of this research area.

Results: MFI-type zeolites belong to a class of prominent nanoporous materials. Even though they are used as catalysts in various applications, many of their features are still not fully understood. An open question concerns the existence of particular aluminum sites in MFI structures. Recently, several theoretical investigations have indicated certain potentially preferred aluminum positions. However, experimental reports are rare and often inconsistent. Therefore, investigations have been performed with the aim of locating such sites experimentally. Aluminum is generally not evenly distributed over the MFI crystallites (zoning) if certain structure directing agents, such as tetrapropylammonium cations, are used in the synthesis. As a starting point, suitable MFI materials have been synthesized. Crystallographic identification of specific sites in such materials would thus be difficult, since diffraction methods result in averaged structure models. To avoid that problem, MFI crystals have been synthesized with a homogeneous aluminum distribution from template-free synthesis gels. Electron microprobe investigations verified the homogeneous aluminum distribution. Silicon and aluminum cannot be distinguished in XRD experiments and also neutron diffraction experiments did not allow direct identification of specific sites.

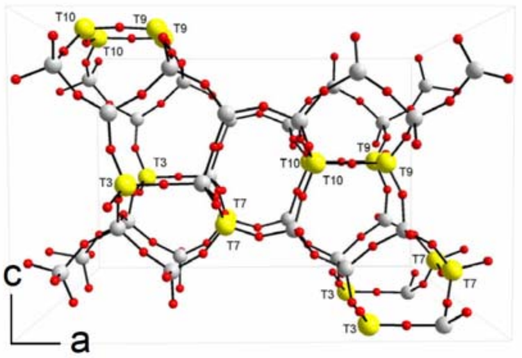

Fig. 1. Representation of the MFI structure. The yellow spheres indicate the sites T3, T7, T9, and T10 which are likely to be occupied by aluminium.

Thus, an indirect method has been chosen. MFI materials consisting of the same parent zeolite that have been exchanged with different cations were examined by X-ray and neutron diffraction. Localization of the extra-framework cations allowed inference on four sites (Figure 1) that have a high probability to be occupied by aluminum. The most probable sites T3, T7, and T9 are accessible in the straight and in the sinusoidal channels of the MFI structure and catalytic conversions would be possible in both channel systems.

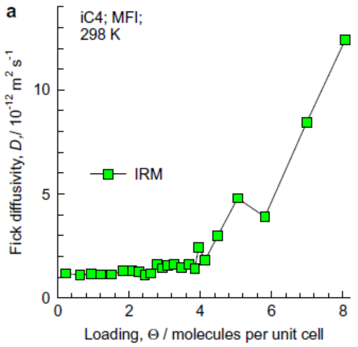

Fig. 2. Diffusivity of *iso*-butane in MFI zeolite at different loadings at 298 K.

Diffusion of molecules in these channels is another factor that determines the catalytic performance of the zeolite. Therefore, diffusion studies of molecules in MFI zeolites have been performed in collaboration with the groups of Kärger, Shah and Krishna. Large (150 µm) and uniform zeolite crystals have been synthesized and investigated. IR and theoretical studies on diffusion of branched alkanes, such as *iso*-butane in MFI, showed the existence of an inflection in the loading dependence of the diffusivity, D, of *iso*-butane. It appears at a loading of four molecules per unit cell, as illustrated in Figure 2. The branched molecules get adsorbed preferentially in the channel intersections (4 per unit cell) and the D is more or less constant for a loading of less than four molecules per unit cell. For higher loadings, inter-molecular repulsion provides the activation energy for a significantly enhanced diffusivity as been shown by KMC simulations.

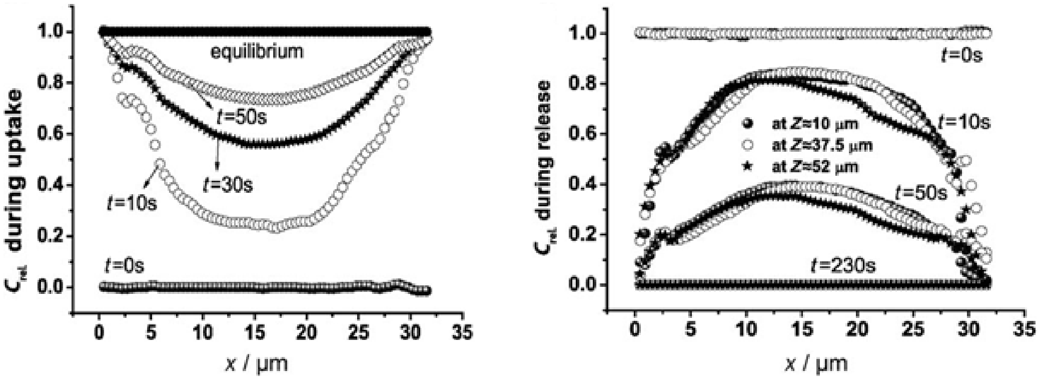

Fig. 3. Time-dependent concentration profiles of 2-methylpropane (isobutane) as a guest molecule in silicalite-1. Evolution of the guest concentration profile along the short x during uptake (left) and release at different z values (right); x being the short, z the long crystal axis.

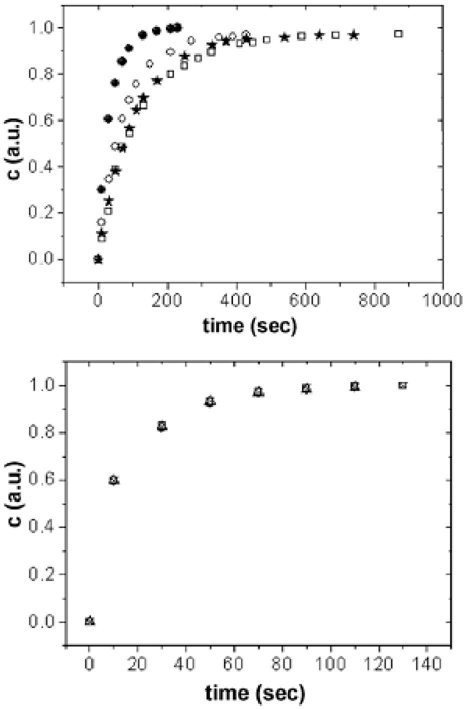

Fig. 4. *iso*-Butane uptake with time on silicalite-1 as observed in four subsequent cycles using iso-butane containing residual water (top) and water-free iso-butane (bottom).

Investigation of molecular diffusion with interference microscopy showed that neither surface barriers nor internal diffusion barriers necessarily exist for well crystallized large MFI crystals. As shown in Figure 3, saturation concentration is achieved close to the crystal surface immediately after exposition of the crystal to the vapor, a clear indication that no external diffusion barrier exists. This has been a rather unexpected discovery. Generally, it was accepted that diffusion barriers are always to be encountered on the surfaces of large MFI crystallites and that stacking faults cause frequent intracrystalline diffusion barriers. In contrast, we could show that for well-crystallized MFI zeolites such transport resistances are negligible if compared to the transport resistance exerted by the zeolite channel systems.

Interestingly, diffusion barriers can be created unwillingly in the course of diffusion experiments if the adsorptive contains residual amounts of water. In that case, successive adsorption of water molecules on the polar external surface of silicalite-1 (i.e., aluminum-free MFI) results in the formation of a surface barrier with increasing exposure time, as indicated in Figure 4 (top). This observation also was rather unexpected and

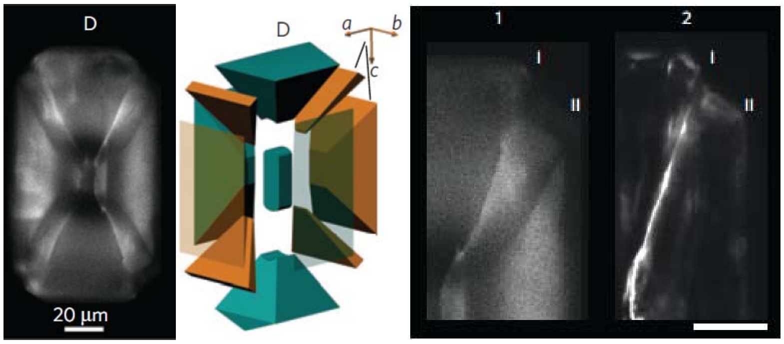

Fig. 5. Confocal fluorescent microscopy images of a twinned MFI-crystal (left) consisting of 5 different types of segments (middle). Fluorescence of stilbene molecules adsorbed at the interface between crystal segments.

showed that specific care has to be taken in the interpretation of diffusion phenomena. The formation of water films on the surface of the zeolite could be avoided using a water trap. As the result subsequent diffusion experiments result in identical uptake curves as illustrated in Figure 4 (bottom).

Different types of diffusion barriers have been observed on MFI crystallites with a rather complex twinning topology, as shown in Figure 5. In cooperation with the Weckhuysen group, rather ill-defined intracrystalline diffusion barriers, consisting of crack-like defects at the interfaces of individual crystal segments have been observed. The existence of rather thin wedge-shaped crystal segments running from the center to the crystal corners, as described in Figure 5 (middle), have been described for the very first time. Large fluorescent dye molecules (stilbene) were able to penetrate and accumulate along these cracks along the interfaces between these thin wedges and neighbor segments, as shown in Figure 5 (right). The defect is observed only on one side of the wedge, no accumulation of dye molecules is observed on the opposite side. Such crystal defects comprise a very specific type of diffusion barriers.

In a survey of NMR signal shapes of alkanes adsorbed on MFI zeolites, ^{1}H NMR signals have been found to be broadened in comparison to alkanes adsorbed on cubic zeolites. Deviations from cubic symmetry apparently does not allow that the dipolar interaction of guests molecules average to zero in MFI zeolites, a fact that is important for the interpretation of PFG NMR data, e.g. in diffusion studies.

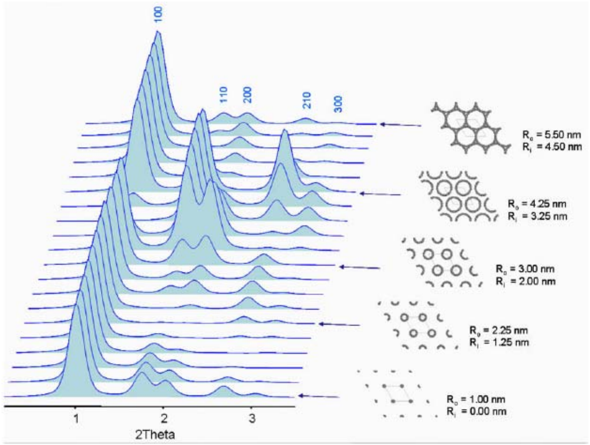

Fig. 6. XRD patterns as calculated from models of CMK-5 carbons.

In the groups of Grünert and Gies novel titanosilicate materials with hexagonally ordered mesopores have been synthesized from MFI-related reaction gels. The properties of these materials have been investigated in a joint collaboration. Even though the investigated materials were not microporous, they had surface properties comparable to those of titananosilicate TS-1 (MFI) and an activity in the epoxidation of cyclohexene that was up to two orders of magnitude higher than that of the TS-1 or Ti-MCM-41 reference materials. The amorphous pore walls most probably consist of motifs comparable to sub-unit cell fragments of TS-1 but with the excessively high surface area of the mesoporous silica, the combination of which explains the high catalytic activity.

Replication of conventional hexagonally ordered mesoporous silica as carbon material results in rod-like CMK-3 or tubular CMK-5 type carbon. Cladding pore walls of SBA-15 with different amounts of carbon yielded carbons with strongly differing XRD patterns. Model building and calculation of theoretical XRD patterns allowed a detailed understanding of X-ray diffraction on such carbons. Minute changes of pore width and/or pore wall thickness of CMK-5 results in significantly different XRD patterns as illustrated in Figure 6. In turn, structural details of CMK-5 could be derived from stepwise optimization of the structure model and least squares optimization of calculated and measured XRD patterns.

An extension of such models in combination with calculation of electron density maps by inverse Fourier Transform methods allowed insight in the adsorption of vapors on CMK-5 carbon. Phase information was derived from structure models whereas structure factors were derived from diffraction intensities that were measured during in-situ XRD measurements during dichloromethane adsorption.

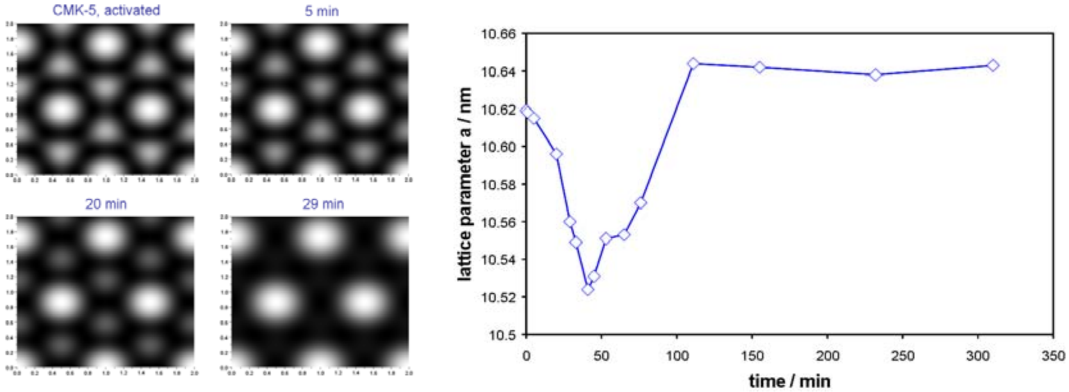

Fig. 7. Electron density maps at different stages of dichloromethane adsorption on CMK-5 (left) and change of lattice parameter during exposure to the vapor (right).

As shown in Figure 7, the adsorption of dichloromethane is a dynamic process. At low loadings it proceeds preferentially in the interstitial pores of CMK-5. During that process the array of carbon tubes contracts, probably as the result of very high capillary forces. After filling of the pores between the tubes, adsorption continues in the tubular pores, accompanied by an expansion of the CMK-5 structure. The distances between the tubes are expanded to an extent that exceeds those that have been observed prior the vapor adsorption. Once all pores are filled, no further structural changes occur, further adsorption then proceeds only at the external surfaces of the carbon particles. The investigations revealed an unexpected flexibility of the CMK-5 pore system.

Publications resulting from this research area: 19, 79, 100, 131, 132, 192, 226, 254, 389, 394

External funding: Deutsche Forschungsgemeinschaft; Elettra Synchrotron Light Source (Trieste, IT)

Cooperations: J. Kärger, C. Chmelik, D. Tzoulaki, D. Freude (Leipzig, DE); H. Jobic (Lyon, FR); D. B. Shah (Cleveland, USA); R. Krishna (Amsterdam, NL); B. Weckhuysen (Utrecht, NL); V. Kahlenberg (Innsbruck, AT); H. Amenitsch (Graz, AT); F. Dreisbach, H. Gies, W. Grünert, A. Puls (Bochum, DE); A.-H. Lu (Dalian, CN); F. Schüth (Mülheim/Ruhr, DE)

2.3.9 Research Area "High-Throughput Multiplexing Chromatography"

(O. Trapp)

Involved: S. K. Weber, S. Bauch, W. Hofstadt

Objective: Continuous real-time sampling in parallelized high-throughput assays is desirable to perform kinetic studies of catalysts or to detect activation and deactivation processes. However, this is often restricted to single-batch systems or has to be performed sequentially. Like in continuous wave spectroscopy the overall duty cycle of chromatographic systems is low and typically most of the acquisition time is spent for recording detector noise. Despite these limitations, performing kinetic studies on large catalyst libraries is a much sought-after objective to get conclusive insights into reaction mechanisms for future developments of advanced materials and catalysts. The major challenge is to increase the duty cycle of the separation system in order to maximize information and minimize analysis time. In this group of projects we continue developing a novel technique combining information technology and chemical analysis.

Results: Combination of information technology and separation sciences opens a new avenue to achieve high sample throughputs and therefore is of great interest to bypass bottle necks in catalyst screening of parallelized reactors or using multitier well plates in reaction optimization. Multiplexing gas chromatography utilizes pseudo-random injection sequences derived from Hadamard matrices to perform rapid sample injections which gives a convoluted chromatogram containing the information of a single sample or of several samples with similar analyte composition. The conventional chromatogram is obtained by application of the Hadamard transform using the known injection sequence or in case of several samples an averaged transformed chromatogram is obtained which can be used in a Gauss-Jordan deconvolution procedure to obtain all single chromatograms of the individual samples. The performance of such a system depends on the modulation precision and on the parameters, e.g. the sequence length and modulation interval. In continuation of our previous studies we could demonstrate the effects of the sequence length and modulation interval on the deconvoluted chromatogram, peak shapes and peak integration for sequences between 9-bit (511 elements) and 13-bit (8191 elements) and modulation intervals Δt between 5s and 500ms using a mixture of five components.

It could be demonstrated that even for high speed modulation at time intervals of 500 ms the chromatographic information is very well preserved and that the separation efficiency can be improved by very narrow sample injections. Furthermore we were able to show that the relative peak areas in multiplexed chromatograms do not deviate from conventionally recorded chromatograms.

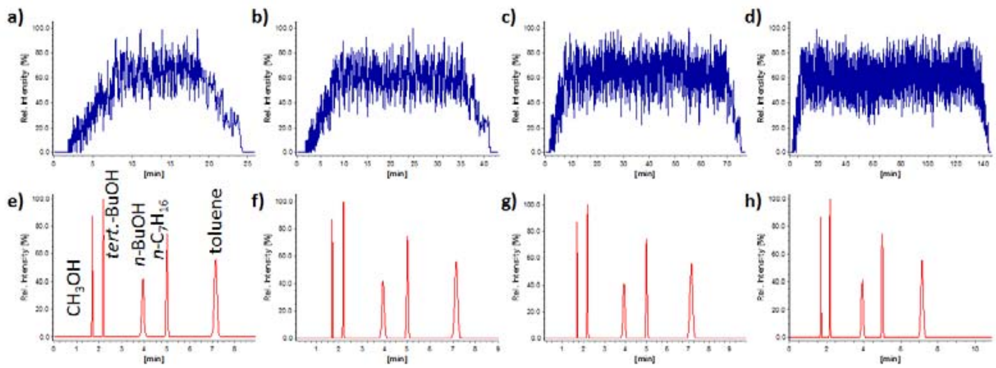

Fig. 1. Multiplexed gas chromatograms (a-d) and Hadamard transformed gas chromatograms (e-h) obtained by injection at a time interval of Δt = 1s and variation of the sequence length. a) 10-bit; b) 11-bit; c) 12-bit; d) 13-bit; e) corresponding transformed chromatogram of a); f) corresponding transformed chromatogram of b); g) corresponding transformed chromatogram of c); h) corresponding transformed chromatogram of d). 25 m fs-capillary (i.d. 250 µm), coated with 500 nm SE-30, isothermal conditions at 50°C, 80 kPa He as inert carrier gas.

Investigations were performed using sample mixture consisting of methanol, *tert*-butanol, *n*-butanol, *n*-heptane and toluene, which were injected into the GC according to *n*-bit binary pseudo-random sequences which are derived from $(n+1) \times (n+1)$ Hadamard matrices. With the newly developed and improved injection valve very well modulated gas chromatograms were obtained. The sequence length was systematically changed from 10-bit 1023 (elements) to 13-bit (8191 elements) and modulation intervals were set between 5s and 600ms. In the same study we also performed a detailed error analysis. Longer modulation sequences are of advantage over short sequences, because small injection fluctuations are compensated, have only a minor impact on the peak areas and the SNR is improved. In particular an average experimental improvement of the SNR of 1.2 for 10-bit sequences, 1.7 for 11-bit sequences, 2.4 for 12-bit sequences and 3.2 for 13-bit sequences compared to 9-bit sequences was observed.

Another highly interesting finding was that with increasing modulation speed (600 ms!) the encoded information in the chromatogram is still conserved.

Furthermore a 4-port multiplexing injector was designed and built for high-throughput screening of 96-well plates. Therefore a high-speed autosampler was built with two xyz axes, the electronics was extended and software to control this machine written.

Publications resulting from this research area: 123, 124

External funding: Deutsche Forschungsgemeinschaft (Emmy Noether Program); Fonds der Chemischen Industrie; Merck Research Laboratories

Cooperations: M. T. Reetz, F. Schüth (Mülheim/Ruhr, DE); R. N. Zare (Stanford, USA)

2.3.10 Research Area “High-Throughput Dynamic Chromatography and On-column Reaction Chromatography” (O. Trapp)

Involved: S. K. Weber, S. Bauch, H.-W. Hofstadt, B. Spliethoff

Objective: Integration of reactions and analysis at the same time opens a new avenue in detailed kinetic screening of catalytic reactions to gain insights into the reaction mechanism on a molecular level. In this group of projects we continue to explore our strategy, which truly unites synthesis and analysis by combining catalytic activity and separation selectivity in the polymeric stationary phase of a chromatographic separation capillary. This was made possible by the derivation of the unified equation which overcame expensive and very slow calculations of reaction rate constants. On-column reaction chromatography is investigated to develop a robust high-throughput system for kinetic and mechanistic investigations of catalytic processes. Several approaches are developed to dissolve or chemically anchor catalysts on polysiloxane matrices. Furthermore the stereodynamics of molecules is investigated in a high-throughput fashion with various separation techniques.

Results: The hydrogenation of 1-acetylcyclohexene, cyclohex-2-enone, nitrobenzene and trans-methylpent-3-enoate catalyzed by highly active palladium nanoparticles was studied by high-throughput on-column reaction gas chromatography. In these experiments catalysis and separation of substrates and products is integrated by the use of a catalytically active gas chromatographic stationary phase which allows to efficiently perform reaction rate measurements employing reactant libraries. Palladium nanoparticles embedded in a stabilizing polysiloxane matrix serve as catalyst and selective chromatographic stationary phase for these multiphase reactions (gas-liquid-solid) and are coated in fused-silica capillaries (i. d. 250 µm) as a thin film of 250 nm. The palladium nanoparticles were prepared by reduction of palladium acetate with hydridomethylsiloxane-dimethylsiloxane copolymer and self-catalyzed hydrosilylation with methylvinylsiloxane-dimethylsiloxane copolymer to obtain a stabilizing matrix. Diphenylsiloxane-dimethylsiloxane copolymer (GE SE 52) was added to improve film stability over a wide range of compositions.

We observed by TEM measurements that size and morphology of the Pd nanoparticles depend on the ratio of the stabilizing polymers, the activation conditions (under hydrogen atmosphere, temperature) as well as on the concentration of the Pd precursor.

The obtained Pd nanoparticles stabilized by a 3:1 ratio of the two polysiloxanes (HMPS:MVPS) are spherical and crystalline with a narrow size distribution of 3.2 ± 0.7 nm determined by TEM. After treatment with hydrogen at elevated temperatures (200°C) we found also amorphous nanoparticles with an increased size of 3.6 ± 1.6 nm, which can be attributed to the formation of Pd hydride and also agglomeration processes at these elevated temperatures. Surprisingly, the size is also controlled by the ratio of the two polysiloxanes. To study this effect systematically we prepared 40 Pd nanoparticles samples by variation of both the mixture of the two polysiloxanes as well as the Pd loadings.

The size distribution of the nanoparticles measured by TEM for five selected ratios of the two stabilizing polysiloxanes (HMPS:MVPS = 1:11, 1:2, 1:1, 2:1, 11:1) indicates that a 1:2 mixture of the two polysiloxanes leads to smaller Pd nanoparticles with a narrow size distribution.

Pd nanoparticles prepared with a polysiloxane ratio of HMPS:MVPS = 1:11 show an increased particle size and a broader size distribution. To study the effect of hydrogen on the size and morphology of the Pd nanoparticles, Cu grids for TEM analysis were coated with the viscous brownish-grey polysiloxanes and then treated with hydrogen at 200°C. It was found that high HMPS and low MVPS concentrations and vice versa as well as high Pd precursor concentrations lead to pronounced agglomeration of the particles with a broad size distribution (11.0 ± 6.2 nm) (cf. Table 1).

The dependency on particle size and distribution of the two polysiloxanes in the particle formation can be explained by kinetic effects. The reduction of Pd^{2+} to Pd^0 is a fast process compared to the hydrosilylation leading to cross-linking and stabilization of the nanoparticles. It can be assumed that in a first step seeds of small Pd nanoparticles are formed which agglomerate to form the resulting nanoparticles. This process is controlled by diffusion. The here used MVPS is compared to HMPS less viscous which should allow easier diffusion of the nanoparticles resulting in the observed agglomeration to larger particles. Samples prepared with a high HMPS concentrations form quickly Pd nanoparticles which can be observed by darkening of the solution. The agglomeration itself is controlled by diffusion and by the rate of the cross-linking of the two polysiloxanes, which dynamically increases the viscosity and decreases diffusion of the particles.

To perform the kinetic investigations of the hydrogenation over the here prepared Pd nanoparticles, solutions of the polysiloxanes with the embedded Pd nanoparticles were used to coat fused-silica capillaries (i. d. 250 µm, 250 nm film thickness) by the static method. For the activation of the Pd nanoparticles and to permanently bond the polysiloxanes to the fused-silica capillary by reaction of surface silanol groups with remaining hydridosiloxane groups the fused-silica capillaries were heated to 200°C at a temperature rate of 0.5 K/ min under slow hydrogen flow. It was found that polymers prepared with an excess of HMPS gave more stable films not leading to droplet formation, which indicates destruction of the polymer film. The on-column catalysis experiments were performed by coupling the Pd nanoparticle micro capillaries (length 2.02 cm, 2.90 cm, 3.84 cm, 5.10 cm, 6.15 cm) between a pre-separation capillary (1 m) and a separation column (25 m), which were installed in a gas chromatograph. The purpose of the pre-separation column was to thermally equilibrate the reactants and to spatially separate the substrates of the injected compound library, which enabled high-throughput kinetic investigations due to the absence of competing reactions. Hydrogen gas was used as reactive carrier gas. Reaction substrates and products were detected by flame ionization detection (FID) for quantification and identified by mass spectrometry (quadrupole ion trap MS). The reactant library consisting of four unsaturated and functionalized compounds (1-acetylcyclohexene, cyclohex-2-enone, nitrobenzene and *trans*-methylpent-3-enoate) was simultaneously injected onto this column configuration at different temperatures (60-100°C) and inlet pressures (60-100 kPa) to vary the reaction time and to obtain temperature dependent kinetic data.

By the use of reactant libraries and measuring reaction rate constants of the spatially separated compounds an extraordinary high throughput could be realized.
We also developed a theoretical model and equations for the efficient evaluation of such experiments.

Furthermore we investigated the stereodynamics of catalytically active metal complexes and diaziridines by enantioselective dynamic gas chromatography and electrophoresis.

Publications resulting from this research area: 121, 122, 125, 163, 411

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