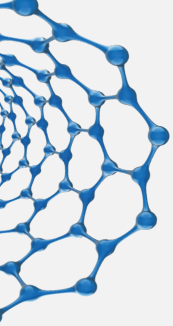
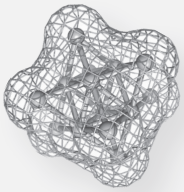
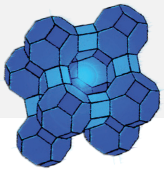




8th International Workshop

Characterization of Porous Materials: From Ångströms to Millimeters

May 6 - 9, 2018 | Delray Beach, FL-USA



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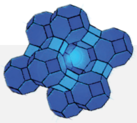

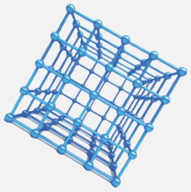

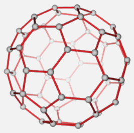

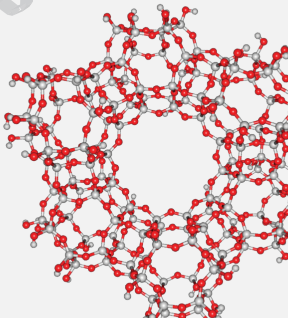

Organizing Committee: Rutgers University and Quantachrome Instruments

Eighth International Workshop
“Characterization of Porous Materials: From Angstroms to Millimeters”

May 6 - May 9. 2018

Workshop Chair: Professor Alexander V. Neimark, Rutgers University

Workshop Vice-Chair: Dr. Matthias Thommes, Quantachrome

The Workshop will provide an opportunity to review and discuss the state-of-the-art approaches to characterize porous materials of different origin. Lectures by recognized leaders in porous materials science will cover both theoretical principles and methodology of modern experimental techniques. Oral presentations and poster sessions will complement invited and keynote lectures. Proceedings will be published as a Special Volume of Colloids and Surfaces A.

International Advisory Committee

Gino Baron, Vrije Universiteit, Brussels, Belgium
Marc-Oliver Coppens, University College London, UK
Renaud Denoyel, University of Provence, Marseille, France

Michael Fröba, Hamburg University, Germany
Alain Fuchs, CNRS, Paris, France
Keith Gubbins, North Carolina State University, USA
Katsumi Kaneko, Shinshu University, Japan
Stefan Kaskel, Technische Universitat Dresden, Germany
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Minoru Myahara, Kyoto University, Japan

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Aix-Marseille University - CNRS, France

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University of Alicante, Spain

Gerhard Findenegg
Technical University Berlin, Germany

Discussion Topics

- **Molecular Thermodynamics of Fluids in Pores**
- **Adsorption and Capillary Phenomena**
- **Intermolecular Interactions in Porous Confinements**
- **Computer Simulations and Density Functional Theory**
- **Energetic Heterogeneity of Surfaces**
- **Fractal Characterization of Disordered Structures**
- **Adsorption Porosimetry of Micro and Mesoporous Solids**
- **Mercury Porosimetry and Liquid Intrusion Techniques**
- **Thermoporometry and Calorimetry**
- **Chromatographic Characterization of Porous Materials**
- **High Resolution Microscopy and Image Analysis**
- **Scattering Techniques for Pore Structure Analysis**
- **Relations Between Structural, Transport, and Functional Properties**

From the Organizers

On behalf of the Organizing Committee, we would like to welcome the advisory committee members, lecturers, and participants of the 8th International Workshop "*Characterization of Porous Materials: from Angstroms to Millimeters*" – **CPM-8** at the Delray Beach Marriott hotel in Delray Beach, Florida, USA, on May 6 - 9, 2018. This Workshop is organized in a similar manner as the previous meetings in the CPM series held in Princeton in 1997, 2000, 2003, 2006, New Brunswick in 2009, and in Delray Beach in 2012 and 2015. Designed to serve a bridge between academics and industrial scientists, CPM Workshops have gained an international reputation for their high-quality interdisciplinary program, interactive style of presentations, and vivid discussions. With the participants representing 26 countries from five continents, CPM-8 is one of the central international events in the subject area in 2018!

The Workshop program includes 9 invited keynote lectures, 4 invited talks in the dedicated industrial session, 45 oral presentations, and 90+ posters, which address topical problems in the experimental, theoretical, and simulation methods of characterization of structural, transport, and functional properties of porous materials of various origins.

The range of practical applications includes regular, disordered, and hierarchical nanostructured materials used as adsorbents, catalysts, drug carriers, and membranes, as well as natural nanoporous systems like shale and other geomaterials.

In addition to the session program, Quantachrome Instruments will host two social events after the conclusion of the workshop on Wednesday afternoon, May 6th: a lab tour of the Quantachrome facilities in Boynton Beach will be followed by an evening cruise aboard the Lady Atlantic.

The CPM-8 papers selected through a rigorous peer-review process will be published as a **Special Issue of Microporous and Mesoporous Materials**, following a tradition of previous CPM Workshops, whose proceedings were published in the special issues of Advances in Colloid and Interface Science, vol. 76-77, 1998, and Colloids and Surfaces A, vol.187-188, 2001, vol. 241, 2004, vol. 300, 2007, vol. 357, 2010, vol. 437, 2013, and vol. 496, 2016.

The submission website is now open at the Elsevier Editorial System and ready for article submission. It is located at https://ees.elsevier.com/micmat/. To ensure that all manuscripts are correctly identified for inclusion into the special issue you are editing, it is important that authors select "SI: CPM-8 proceedings" when reaching the "*Article Type*" step in the submission process. Note that we intend to publish the full scale concise articles of the highest quality; abbreviated versions will not be considered. Please strictly follow the guidelines for manuscript preparation and submission posted on the journal website at: https://www.elsevier.com/journals/microporous-and-mesoporous-materials/1387-1811/guide-for-authors. The deadline for manuscript submission is May 31, 2018. Our plan is to complete peer-review over the summer and to publish the special issue in October 2018.

We are looking forward to an exciting and fruitful meeting.

With warm wishes,

Alex Neimark, Workshop Chair
Rutgers University,
Piscataway, New Jersey

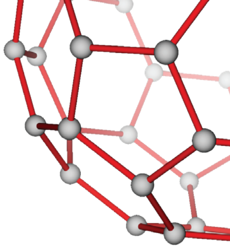
Matthias Thommes, Workshop Vice-Chair
Quantachrome Instruments,
Boynton Beach, Florida

Sunday, May 6, 2018
1:30 p.m. Opening

1:30 - 2:00 PM	Opening Remarks: **Alexander V. Neimark**- Workshop Chair (Rutgers University, United States) and **Matthias Thommes**- Workshop Vice-Chair (Quantachrome Instruments, United States), **Keith Gubbins**, North Carolina State University, United States

2:00 p.m. Session: Effects of Nanoconfinements
Chair: Keith Gubbins

2:00 - 2:30 PM	Keynote Lecture - **Katsumi Kaneko** ***Nanoconfinement Mediated Materials / Adsorption Engineering*** Shinshu University, Japan
2:30 - 2:50 PM	**Michael Froeba**, Benedikt Mietner, Young Joo Lee, Sandra Koenig, Uta Sazama, and Felix Brieler ***Properties of Water Confined in Periodic Mesoporous Organosilicas: Nanoimprinting The Local Structure*** University of Hamburg, Germany
2:50 - 3:10 PM	**Michael Hirscher**[1], Rafael Balderas-Xicohténcatl[1] , Katie A. Cychosz[2] , Remy Guillet-Nicolas[2] , Luke L. Daemen[3] , Yong Q.Cheng[3] , Anibal J. Ramirez-Cuesta[3] , Hung-Hsuan Lin[4] , Thomas Heine[4] and Matthias Thommes[2] ***Density of Adsorbed Hydrogen at Low Temperatures in Mesoporous Materials*** [1] Max Planck Institute for Intelligent Systems, Germany, [2] Quantachrome Instruments, United States, [3] Spallation Neutron Source, United States, [4]Leipzig University, Germany
3:10 - 3:30 PM	**Rustem Valiullin**, Daniel Schneider and Daria Kondrashova ***Phase Transitions in Geometrically Disordered Mesoporous Solids*** University of Leipzig, Germany
3:30 - 3:50 PM	**Pierre Levitz** ***Probing Interfacial Water Dynamics in Colloidal and Nanoporous Systems by Nuclear Magnetic Relaxation Dispersion*** CNRS/UPMC, France
3:50 - 4:10 PM	**Break**



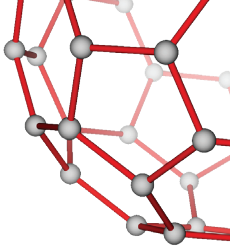
CPM8 | PROGRAM

Sunday, May 6, 2018
4:10 p.m. Session: Nanoporous Materials and Adsorption Processes for Industrial Applications
Chair: Peter Ravikovitch

4:10 - 4:35 PM	Invited Talk - **Robert Bedard** ***New SAPO based nanoporous materials and some potential applications*** Honeywell UOP, United States
4:35 - 5:00 PM	Invited Talk - **Christian Canlas**, Kevin Sutovich, Jane Dowell, Andrew Lim, Renee Foard, Hui Jiang, Mike Ziebarth and Wu-Cheng Cheng ***Porosimetry: Applications and Challenges in Fluid Catalytic Cracking*** W. R. Grace & Co., United States
5:00 - 5:25 PM	Invited Talk - **Nikolai Nesterenko** ***From Molecular Sieves to Industrial Catalysts: The Past, Present & Future in Total*** Total S.A., Belgium
5:25 - 5:50 PM	Invited Talk - **Andrew Pomerantz** ***Kerogen-Hosted Porosity: Controls on Storage and Transport in Gas Shale*** Schlumberger-Doll Research, United States
5:50 - 6:10 PM	**Pegie Cool**[1], Qi Xin1, Vera Meynen[1], A. Papavasiliou[2] and F.K. Katsaros[2] ***Water-Based Route Towards Dispersed CuO-Loaded Catalysts: Texture, Structure and Catalytic Performance in Automotive Exhaust Gas Conversion*** [1]University of Antwerp, Belgium, [2]National Center for Scientific Research “Demokritos”, Greece
6:10 - 6:30 PM	**Federico Brandani**[1], Pluton Pullumbi[1], Stefano Brandani[2] and Enzo Mangano[2], ***Characterizing The Mass Transfer Kinetic Mechanism In Microporous Adsorbents Using The Volumetric Technique*** [1]Air Liquide Center de Recherche Paris-Saclay, France, [2]University of Edinburgh
7:00 PM	**Welcome Reception**

Monday, May 7, 2018
8:30 a.m. Session: Characterization of Pore Structure and Confined Fluids
Chair: Katsumi Kaneko

8:30 - 9:00 AM	Keynote Lecture - **Gerhard H. Findenegg** ***Structural Characterization Of Complex Fluids In Tubular Nanopores*** Technical University of Berlin, Germany
9:00 - 9:20 AM	**Michael Steiger**, Tanya Talreja and Kristen Linnow ***Deliquescence of NaCl Crystals in Confinement*** University of Hamburg, Germany
9:20 - 9:40 AM	**Simone Mascotto**[1], Giorgia Greco[2], Eike Gerike[1], Dirk Wallacher[2], Armin Hoell[2], Michael Krumrey[3], Klaus Rademann[4] and Simone Raoux[2] ***Direct Investigation of The Adsorbate Evolution in Mesoporous Silicon Combining Anomalous SAXS, EXAFS and Xenon Physisorption*** [1]University of Hamburg, Germany, [2]Helmholtz-Zentrum Berlin, Germany, [3]Physikalisch - Technische Bundesanstalt Institute Berlin, Germany, [4]Institut für Chemie, Humboldt-Universität zu Berlin, Germany
9:40 - 10:00 AM	**Patrick Huber**[1], Mark Busch[1], Kathrin Sentker[1], Tommy Hofmann[2], Dirk Wallacher[2], Andriy V. Kityk[3,1], Andreas Schönhals[4], Arda Yildirim[4], Arne Zantop[5] and Marco Mazza[5] ***Liquid Crystals Confined In Mesopores: Adsorption Isotherms, Self-Assembly of Supermolecular Helices and Extremely Fast Electro-Optics*** [1]Hamburg University of Technology, Germany, [2]Helmholtz Center Berlin for Materials and Energy, Germany, [3]Czestochowa University of Technology,Poland, [4]Federal Institute for Materials Research and Testing, Germany, [5]Max-Planck Institute for Dynamics and Self-Organization,Germany.
10:00 - 10:20 AM	**Mirian Elizabeth Casco**, En Zhang, Sven Grätz, Volodymyr Bon, Simon Krause, and Lars Borchardt ***Impact of The Surface Chemistry on The Methane Hydrate Formation In Carbon Nanopores*** TU Dresden, Germany
10:20 - 10:50 AM	**Break**

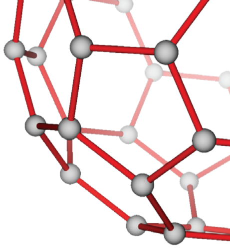


Monday, May 7, 2018
10:50 a.m Session: Molecular Simulations
Chair: Alain Fuchs

10:50 - 11:20 AM	Keynote Lecture - **Keith Gubbins** ***Compression and high pressure effects in adsorbed films*** North Carolina State University, United States
11:20 - 11:40 AM	**Daniel W Siderius**, Nathan A. Mahynski, and Vincent K. Shen ***Calculation of The Isosteric Enthalpy of Adsorption In Monte Carlo Molecular Simulation: Consideration of Bulk Phase Nonideality and Isosteres of Total Adsorption*** National Institute of Standards and Technology, United States
11:40 - 12:00 PM	**J. Ilja Siepmann**[1,2], Evgenii O. Fetisov, Mansi S. Shah[1,2] and Michael Tsapatsis,[1] ***First Principles Monte Carlo Simulations of Adsorption and Reaction Equilibria*** [1]Department of Chemical Engineering and Materials Science, University of Minnesota, United States, [2]Department of Chemistry and Chemical Theory Center, University of Minnesota, United States
12:00 - 12:20 PM	**Jacek Jagiello**[1], and Mietek Jaroniec[2] ***Adsorption Model for Porous Oxides with Corrugated Cylindrical Pores 2D-NLDFT Approach*** [1]Micromeritics Instrument Corporation, United States, [2]Kent State University, United States
12:20 - 12:40 PM	**Tatsumasa Hiratsuka**, Hideki Tanaka and Minoru Miyahara ***Comprehensive Modeling of Capillary Condensation/Evaporation in Open-Ended Nanopores*** Kyoto University, Japan
12:40 - 2:10 PM	**Lunch Break**

Monday, May 7, 2018
2:10 p.m. Session: Advanced Materials
Chair: Joeri Denayer

2:10 - 2:40 PM	Keynote Lecture - **Peter Behrens** ***Nanoporous Biomaterials*** University of Hanover, Germany
2:40 - 3:00 PM	**Bernd Smarsly**[1], Torben Pfaff[1], Felix Badaczewski[1], Marc Loeh[1] and Dirk Wallacher[2] ***Small-Angle Neutron Scattering (SANS) of Porous Carbons Combined with in-situ Physisorption Measurements – Linking Microstructure to Nanoscaled Porosity*** [1]University of Giessen, Germany, [2]Berlin Neutron Scattering Center, Germany
3:00 - 3:20 PM	**Teresa J Bandosz**, and Dimitrios Giannakoudakis ***Smart Cotton Textiles for detection/detoxification of nerve agents: role of MOF/g-C3N4 features*** The City College of New York, United States
3:20 - 3:40 PM	**Remy Guillet-Nicolas**[1,2,3], François Bérubé[3], Matthias Thommes[2], Michael T. Janicke[4] and Freddy Kleitz[*1,3] ***Selectively Tuned Pore Condensation and Hysteresis Behavior in Mesoporous SBA-15 Silica: Correlating Material Synthesis to Advanced Gas Adsorption*** [1]University of Vienna, Austria, [2]Quantachrome Instruments, United States, [3]Université Laval, Canada, [4]Los Alamos National Laboratory, United States.
3:40 - 4:00 PM	**Michael Tiemann**, Christian Weinberger, Sai Ren, Xiaojuan Cao, Marc Hartmann, and Thorsten Wagner ***Bimodal Mesoporous CMK-5 Carbon: Selective Pore modification and Pore Filling*** University of Paderborn, Germany
4:00 - 4:20 PM	**Lars Borchardt**, Desiree Leistenschneider, Sven Grätz and Christina Schneidermann ***Syntheses in Ball Mills – Solvent Free Pathways Towards Porous Carbons and Polymer Frameworks*** Technische Universität Dresden, Germany
4:20 - 4:40 PM	**Break**
4:40 - 7:30 PM	**Poster Session**



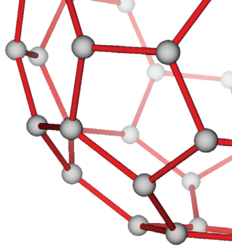
CPM8 | PROGRAM

Tuesday, May 8, 2018
8:30 a.m. Session: Molecular Modeling
Chair: Peter Monson

8:30 - 9:00 AM	Keynote Lecture - **Alain Fuchs** ***Forced Intrusion of Water and Aqueous Solutions in Nanoporous Materials*** PSL University - Paris, France
9:00 - 9:20 AM	**Duong Dang Do**, Yonghong Zeng, Hui Xu, Arkanata Akram, Luisa Prasetyo, Shiliang Tan and D. Nicholson ***Clusters, Molecular Layers and Condensate in Adsorption: Interplay between various Interactions and the Nature of the Adsorbed Phase-Gas Interface*** University of Queensland, Australia
9:20 - 9:40 AM	**Youn-Sang Bae**, Seo-Yul Kim, Wanje Park, Seung-Ik Kim and Seung-Joon Lee ***A Novel Acetic Acid-Fragment Co-Assembly Method for Creating Defects in a Copper-Based Metal-Organic Framework and Its Effects on Methane Uptakes*** Yonsei University, Republic of Korea
9:40 - 10:00 AM	**Romain Gaillac**[1, 2], François-Xavier Coudert[1] and Pluton Pullumbi[2], ***Modeling of Liquid Metal-Organic Frameworks*** [1]ENSCP/CNRS, France, [2]Air Liquide, Paris-Saclay Research Center, France
10:00 - 10:20 AM	**Benoit Coasne** ***Transport as a Tool to Characterize Multiscale Porous Media*** CNRS/University of Grenoble, France
10:20 - 10:40 AM	**Break**

Tuesday, May 8, 2018
10:40 a.m. Session: Experimental Methods
Chair: Stefano Brandani

10:40 - 11:10 AM	Keynote Lecture - **Conchi Ania**[1], Alicia Gomis-Berenguer[1,2], José B. Parra[2], Eduardo Salas[3] and Germán Castro[3] ***In-situ Synchrotron X-ray Diffraction Upon Gas Adsorption and Release for Exploring Unusual Adsorption Features in Porous Materials*** [1]CEMHTI/CNRS, France, [2]Instituto Nacional del Carbón, Spain, [3]European Synchrotron Radiation Facility, France
11:10 - 11:30 AM	**Joaquin Silvestre Albero**[1], Yonqiang Q. Cheng[2], Luke L. Daemen[2], Anibal J. Ramirez-Cuesta[2] and Carlos Cuadrado-Collados[1] ***Synchrotron XRD and in Elastic Neutron Scattering Studies Under Operando Conditions to Understand Structural Phenomena in ZIFs*** [1]University of Alicante, Spain, [2]Oak Ridge National Laboratory, United States,
11:30 - 11:50 PM	**Steven Claes** and Hans Janssen ***Multi-Scale Pore Network Characterization of Building Materials Using Micro-CT and FIB-SEM Tomography*** KU Leuven, Belgium
11:50 - 12:10 PM	**Margarita Russina**[1], Ewout Kemner[1] and Ferenc Mezei[2,3] ***Probing Potential of The Confinement – Study of In-Cage Dynamics of Molecular Hydrogen in Clathrates Hydrates.*** [1]Helmholtz-Zentrum Berlin, Germany, [2]European Spallation Source, Sweden, [3]Wigner Research Center for Physics, Hungary
12:10 - 12:30 PM	**Sean P. Rigby**[2], Galina E. Pavlovskaya[1], Thomas Meersmann[1] and Chunyu jin[1] ***Fluid Flow and Permeation Within a Hierarchical Porous Medium With Transverse Permeability Discontinuity*** [1] Sir Peter Mansfield Imaging Centre, School of Medicine, University of Nottingham, United Kingdom [2] Department of Chemical and Environmental Engineering, University of Nottingham, United Kingdom
12:30 - 12:50 PM	**Dieter Bathen**[1], Christian Bläker[1], Christoph Pasel[1] and Frieder Dreisbach[2] ***Coupling of Volumetric and Calorimetric Devices for Simultaneous Measurements of Adsorption Isotherms and Enthalpies*** [1]University of Duisburg-Essen, Germany, [2]Rubotherm GmbH, Germany
12:50 - 2:10 PM	**Lunch Break**

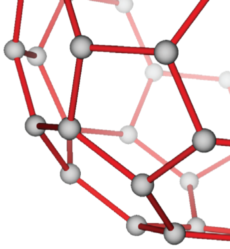


Tuesday, May 8, 2018
2:10 p.m. Session: Experimental Methods II
Chair: Bernd Smarsly

2:10 - 2:30 PM	**Ryusuke Futamura**[1], Taku Liyama[1], Yury Gogotsi[1,2], Mark J. Biggs[3,6], Mathieu Salanne[4], Patrice Simon[1,5] and Katsumi Kaneko[1] ***Pore Size Effects on Partial Breaking of Coulombic Ordering Structure of Ionic Liquids in Carbon Nanopores*** [1]Shinshu University, Japan 2Drexel University, United States, [3]Loughborough University, United Kingdom, [4]Sorbonne Universités, France, [5]Université Paul Sabatier, [6]The University of Adelaide, Australia
2:30 - 2:50 PM	**Lisa Joss** and Ronny Pini ***X-ray CT Imaging of Gas Adsorption to Characterize Nanoporous Materials*** Imperial College London, United Kingdom
2:50 - 3:10 PM	**Marta Falkowska**[1], Daniel T. Bowron[2], Haresh Manyar[3], Tristan G.A. Youngs[2] and Chris Hardacre[1] ***What Effect Does Confinement Have on The Structure of Liquid Benzene?*** [1]The University of Manchester, United Kingdom, [2]STFC ISIS Facility, Rutherford Appleton Laboratory, United Kingdom, [3] School of Chemistry and Chemical Engineering Queen's University Belfast, United Kingdom
3:10 - 3:30 PM	**Joeri Denayer**, Julien Cousin Saint Remi, Stijn Van der Perre, Benjamin Claessens and Gino Baron ***Size-Controllable MOF Composite Particles for Adsorptive Separations: Formulation, Characterization and Study of Mass Transfer Resistances*** Vrije Universiteit Brussel, Belgium
3:30 - 3:50 PM	**Emily Bloch**[1], Nicolas Chanut[1], Sandrine Bourrelly[1], Bogdan Kuchta[1], Christian Serre[2], Jong-San Chang[3,4], Paul A. Wright[5] and Philip L. Llewellyn[1] ***An Experimental Method for Screening the Effect of Water Vapour on Gas Adsorption Performance: Application to CO2 Capture From Flue Gas in MOFs*** [1]Aix-Marseille University/CNRS, France, [2]ESPCI Paris, ENS,, France, [3]Departement of Chemistry Sungkyunkwan University, Korea, [4]Research Center for Nanocatalysts, Korea, [5]University St Andrews, Scotland
3:50 - 4:10 PM	**Paola Rodríguez**[1], Juan Carlos Moreno Piraján[1] and Liliana Giraldo [2] ***Immersion Calorimetry Study of Textural and Chemical Modifications of MOFs*** [1]University of Los Andes, Colombia, [2] Universidad Nacional de Colombia, Colombia,
4:10 - 4:30 PM	**Break**

Tuesday, May 8, 2018
4:30 p.m. Session: Adsorption Deformation
Chair: Joaquin Silvestre Albero

4:30 - 5:00 PM	Keynote Lecture - **Oskar Paris** ***Assessing Adsorption Induced Deformation of Nanoporous Materials with X-ray and Neutron Scattering*** University in Leoben, Austria
5:00 - 5:20 PM	**Robert Eschrich**[1], Christian Reichenbach1, Andreas Möller[1], Jen Möllmer[2], Marcus Lange[2], Hannes Preißler[2], Roger Gläser[2] and Matthias Thommes[3] ***Flexible MOFs for Gas Separation – A Case Study Based on Static and Dynamic Sorption Experiments.*** [1]Quantachrome GmbH & Co. KG, Germany, [2]Institut für Nichtklassische Chemie e.V., [3]Quantachrome Instruments, FL , United States
5:20 - 5:40 PM	**Bogdan Kuchta**[1,3], Lucyna Firlej[2,3], Filip Formalik[4] and Philip Llewellyn[1] ***Structural Transformations of Methane Adsorbed in MOF-5 Model Framework*** [1]Aix-Marseille University, France, [2]University of Montpellier, France, [3]University of Missouri, United States, [4]Wroclaw University of Science and Technology, Poland
5:40 - 6:00 PM	**Carlos Wexler**, Joseph Schaeperkoetter, Helmut Kaiser and Haskell Taub ***In-situ Neutron Scattering Observation of Adsorption-Induced Expansion in the Interlayer Spacing of Graphene Oxide Frameworks*** University of Missouri, United States
6:00 - 6:20 PM	**Christian Lastoskie** and Francisco J. Sotomayor ***Prediction of Carbon Dioxide Breakthrough in "Gating" Adsorbents Using Osmotic Framework Adsorbed Solution Theory*** University of Michigan, United States
6:20 - 6:40 PM	**Irena Senkovska**[1], Alexander Krylov[2], Alexander Vtyurin[2,3], Petko Petkov[4,5], Mariia Maliuta[1], Volodymyr Bon[1], Thomas Heine[4], Stefan Kaskel[1] and Evgenia Slyusareva[3] ***Raman Spectroscopy Studies of the Terahertz Vibrational Modes of Flexible Pillared Layer MOF*** [1]Technische Universität Dresden, Germany, [2] Federal Research Center KSC SB RAS, Russia, [3]Siberian Federal University, Russia, [4]University of Sofia, Bulgaria, [5]Universität Leipzig, Germany
8:00 PM	**Conference dinner**



Wednesday, May 9, 2018
9:00 a.m. Session: Dynamics and Diffusion
Chair: Duong D. Do

9:00 - 9:30 AM	Keynote Lecture - **Peter Monson** ***Modeling Dynamics of Confined Fluids: From Adsorption to Membrane Separations*** University of Massachusetts - Amherst, United States
9:30 - 9:50 AM	**Stefano Brandani** and Alessio Centineo ***Measurement of Water Adsorption Equilibrium and Kinetics Using the ZLC Technique*** University of Edinburgh, United Kingdom
9:50 - 10:10 AM	**Gennady Y. Gor**[1] and Boris Gurevich[2] ***How to Interpret Ultrasonic Measurements on Fluid-Saturated Nanoporous Solids?*** [1]New Jersey Institute of Technology, United States, [2]Curtin University and CSIRO Australia
10:10 - 10:30 AM	**István Furó**[1], Fredrik Elwinger[2] and Payam Pourmand[1] ***Diffusive Transport in Pores. Tortuosity and Molecular Interaction with the Pore Wall*** [1]KTH Royal Institute of Technology, Sweden, [2]GE Healthcare Bio-Sciences AB, Sweden
10:30 - 10:50 AM	**Break**

Wednesday, May 9, 2018
10:50 a.m. Session: Metal-Organic Frameworks
Chair: Michael Froeba

10:50 - 11:20 AM	Keynote Lecture - **Jeffrey Long**[1], Rebecca Siegelman[1,3], Douglas Reed[1], Jonathan Bachman[2], Phillip Milner[1,3], Miguel Gonzalez[1], Julia Oktawiec[1], Lucy Darago[1], Tomče Runčevski[1], Jeffrey Martell[1], Dianne Xiao[1], Thomas McDonald[1], Jarad Mason[1], Eric Bloch[1], Zoey Herm[1], Benjamin Keitz[1], Brian Wiers[1], Wendy Queen[1,3], Stephen Geier[1] and Leslie Murray[1] ***Cooperative Adsorption and Gas Separations In Metal-Organic Frameworks*** [1]Departments of Chemistry, University of California, United States, [2]Chemical and Biomolecular Engineering, University of California, United States, [3]Lawrence Berkeley National Laboratory, United States
11:20 - 11:40 AM	**Simon Krause**[1], Volodymyr Bon[1], Irena Senkovska[1] , Daniel M. Többens[2] , Dirk Wallacher[2], Guillaume Maurin[3], François-Xavier Coudert[4] and Stefan Kaskel[1] ***Negative Gas Adsorption in Mesoporous Switchable Metal-Organic Frameworks*** [1]Dresden University of Technology, Germany, [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, [3]Université Montpellier, France, [4]Chimie ParisTech, France
11:40 - 12:00 PM	**Hyunchul Oh**[1], Hoi Ri Moon[2] and Michael Hirscher[3] ***Exploiting Diffusion Barrier and Chemical Affinity of Metal-Organic Frameworks for Efficient Hydrogen Isotope Separation*** [1]GNTECH, Republic of Korea, [2]UNIST, Republic of Korea, [3]Max Planck Institute for Intelligent Systems, Germany
12:00 - 12:20 PM	**T. Grant Glover**[1], Jackson Cunningham[1], Mohammad Hossain, Tim M. Becker[2] and Brooks D. Rabideau[1] ***Binary Adsorption of CO2 and Water on UiO-66 MOF*** [1]University of South Alabama, United States, [2] Delft University of Technology, Netherlands

12:20 p.m Closing

12:20 - 12:50 PM	**Alex Neimark** (Rutgers University, United States)**, Matthias Thommes** (Quantachrome Instruments, United States) and **Gerhard Findenegg** (TU Berlin) ***Discussion and Closing Remarks***

Post-Conference Events (Registration Required)

3:00 - 5:00 PM	**Quantachrome Instruments Tour**
6:00 - 8:30 PM	**Sunset Cruise Sponsored by Quantachrome**

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Funding Opportunities

1 ***Funding Opportunities at NSF's CBET division: Process Systems Cluster***
Angela D. Lueking

National Science Foundation, United States

Characterization of Pore Structure and Confined Fluids

2 ***Characterization of Nuclear Concretes: Effect of Thermal Stress up to 1000°c***
Helena Mastori[1], Michael Antoni[1], Pascal Piluso[2], Jean-François Haquet[2] and R. Denoyel[2]

[1]Aix Marseille University, France, [2] French Atomic Energy and Alternative Energies Commission

3 ***Characterisation of Polymer-based Composites with Enhanced Microporosity for Gas Storage***
Mi Tian, Sébastien Rochat, Katarzyna Polak-Kraś na, Leighton T. Holyfield, Andrew D. Burrows,
Christopher R. Bowen and Timothy J. Mays

University of Bath, United Kingdom

4 ***Absorption Artifacts Upon Analysis of Organic Porous Materials with N2 Adsorption***
Christian Balzer[1], Manual Seitz[1], Matthias Thommes[2] and Gudrun Reichenauer[1]

[1]Bavarian Center for Applied Energy Research, Germany, [2]Quantachrome Instruments, United States

5 ***Pore Size Distribution From Non-Local Density Functional Theory: Evaluation of Adsorption-Isotherm Data Fluctuations***
Amaro Gomes Barreto Jr., Vítor de Morais Sermoud and Frederico W. Tavares

Federal University of Rio de Janeiro, Brazil

6 ***How Dense is the Gas Confined in Nanopores?***
Lucyna Firlej[1,3] , Bogdan Kuchta[2,3] and Katarzyna Walczak[1]

[1]University of Montpellier, France, [1]University Aix-Marseille, France, [3]University of Missouri, United States

7 ***Gas Adsorption Studies on Shales and Gas-In-Place Calculations***
Humera Ansari, Geoffrey Maitland, Ronny Pini and J P Martin Trusler

Imperial College London, United Kingdom

8 ***Artificial Opals as a Model of a Shale Rock: Study of Nanoconfined Oil Combustion***
Andrei Galukhin and Dmitrii N. Bolmatenkov

Kazan Federal University, Russia

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Characterization of Pore Structure and Confined Fluids

9 ***Determination of Microstructural Characteristics of Advanced Biocompatible Nanofibrous Membranes***
Karel Soukup, Vladimir Hejtmanek and Olga Solcova

Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Czech Republic

10 ***Morphology of Living Pore Structure in Microporous Polypropylene film***
Tarakol Hongkeab and Arthorn Wichitamornloet

Enzpire Industry Ltd., Thailand

11 ***Use of Adsorbate Wetting Differences for Structural Characterization***
Sean P. Rigby[1], Muayad Hasan[1,2], Lee Stevens[1] and Huw E.L. Williams[1]

[1]University of Nottingham, United Kingdom, [2]University of Technology, Baghdad, Iraq

12 ***Pore Network Analysis: Interpretation of Hysteresis Scanning Measurements***
König Sandra[1], Katie Cychosz[2], Uta Sazama[1], Jakob Benedikt Mietner[1], Natascha Speil[1], Matthias Thommes[2] and Michael Fröba[1]

[1]University of Hamburg, Germany, [2]Quantachrome Instruments, FL, United States

13 ***Thermodynamic Studies on the Phase Behavior of Water within Periodic Mesoporous Organosilicas (PMOs) with Different Surface Polarities***
Uta Sazama[1], Sandra König[1], Jakob Benedikt Mietner[1], Katie Cychosz[2], Matthias Thommes[2] and Michael Fröba[1]

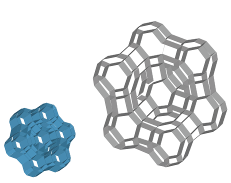
[1]University of Hamburg, Germany, [2]Quantachrome Instruments, FL, United States

14 ***Textural Characterization of Shale Nanostructure***
Katie A. Cychosz[1], Enzo Mangano[3], Drew Pomerantz[2], Stefano Brandani[3] and Matthias Thommes[1]

[1]Quantachrome Instruments, United States, [2] Schlumberger-Doll Research, United States,
[3]University of Edinburgh, United Kingdom

15 ***Pore Size and Porosity Analysis of Meso- and Macroporous Sol-Gel Based Materials by using Electroacoustics***
Matthias Thommes[1], Stephan Braxmeier[2], Max Mundlein[2], Gudrun Reichenauer[2] and A. Dukhin[3]

[1]Quantachrome Instruments, United States, [2]Bavarain Center for Applied Energy Research, Germany,
[3]Dispersion Technology Inc, United States



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Molecular Simulations & Modeling

16 *Molecular Insight on the Behavior of Carbon Dioxide within Zeolites*
Daniela Kohen

Carleton College, United States

17 *Molecular Simulation of CO2 Adsorption for Pore Characterization*
Silvio Dantas[1], Katie Cychosz[2], Matthias Thommes[2] and Alexander Neimark[1]

[1]Rutgers University, United States, [2]Quantachrome Instruments, United States

18 *Pore Structure Characterization of MOF-based Materials by Gas Adsorption*
F. Silvio P. Dantas, and Alexander V. Neimark

Rutgers University, United States

19 *Adsorption of Hydrogen Isotopes in the Zeolite NaX: Experiments and Simulations*
Marcos Salazar

CNRS , France

20 *Compressibility of Nitrogen Adsorbed in Vycor Glass*
Max A. Maximov and Gennady Y. Gor

New Jersey Institute of Technology, United States,

21 *Predictions of Solvation Pressure in Mesopores Based on Saam-Cole Theory*
Alina Emelianova and Gennady Gor

New Jersey Institute of Technology, United States

22 *A Universal Isotherm Model for Adsorption Uptake and Energy Distribution Design of Porous Heterogeneous Surface*
Muhammad Burhan, Muhammad Wakil Shahzad and Kim Choon Ng

King Abdullah University of Science and Technology, Saudi Arabia

23 *Measuring and Modelling Sub- and Supercritical Gas Adsorption on Clays*
Junyoung Hwang and Ronny Pini

Imperial College London, United Kingdom

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Molecular Simulations & Modeling

24 ***Comprehensive Modeling of Capillary Condensation/Evaporation in Open-Ended Nanopores***
Tatsumasa Hiratsuka, Hideki Tanaka and Minoru Miyahara

Kyoto University, Japan

25 ***Pore Size Distribution in Hierarchical Materials: Insights from Molecular Simulations***
J. Ilja Siepmann[1], Mansi S. Shah[1,2], Swagata Parhari[2], Limin Ren[1], Dandan Xu[1], Michael Tsapatsis[1], Katie Cychosz[2] and Matthias Thommes[2]

[1]University of Minnesota, United State, [2]Quantachrome Instruments, United States

26 ***Intrusion of Water and Electrolytes in Hydrophobic Soft Porous Crystals: Some Insights From Molecular Simulation***
Guillaume Fraux and François-Xavier Coudert

Chimie ParisTech-PSL Research University-CNRS Institut de Recherche de Chimie, France

27 ***Computational Study of Vibrational Properties of ZIFs with SOD Topology***
Bogdan Kuchta[1], Filip Formalik[1] and Michael Fischer[2]

[1]Wrocław University of Science and Technology, Poland, [2]University of Bremen, Germany

28 ***Influence of Intermediate Structures of MIL-53 on Adsorption Mechanism***
Justyna Rogacka[1], Azahara Luna Triguero[2], Sofia Calero[2] and Bogdan Kuchta[1,3]

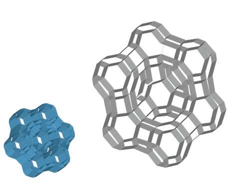
[1]Wrocł aw University of Technology, Poland, [2]University Pablo de Olavide, Spain, [3]Aix-Marseille Université, France

29 ***Disclosing adsorption mechanisms in Zr-based MOFs using a molecular modeling approach***
Andreas M. Schneider, Malte Schäfer and Peter Behrens

Leibniz University Hannover, Germany

30 ***Heterogeneous Multikernel Analysis of Carbon Microstructure***
Sebastiao M.P. Lucena, Jose C.A. Oliveira, Daniel V. Goncalves and Pedro F.G. Silvino

Federal University of Ceara, Brazil



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Molecular Simulations & Modeling

31 ***Conformal Sites Model for Adsorbed Films on Energetically Heterogeneous Surfaces***
Kaihang Shi, Erik Santiso and Keith Gubbins

North Carolina State University, United States

32 ***Heterogeneous Surface Models Obtained by Reactive Molecular Dynamics***
Sebastião M.P. Lucena, Rafael V. Gonçalves, Pedro F.G. Silvino, Daniel V. Gonçalves and Jose C.A. Oliveira

Universidade Federal do Ceara, Brazil

33 ***NIST Data Resources for Cataloging Adsorption Measurements***
Daniel W. Siderius, Vincent K. Shen, Russell D. Johnson III, and Roger D. van Zee

National Institute of Standards and Technology, United States

34 ***pyGAPS: A Python-based General Adsorption Processing Suite***
Paul Adrian Iacomi, and Philip Llewellyn

Laboratoire MADIREL, CNRS/AMU, France

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Advanced Materials: Oxidic

35 ***Catalytic Activity of Desilicated and Modified with Cu Commercial ZSM-5 in Environmental Processes***
Małgorzata Rutkowska[1], Iwona Pacia[1], Sylwia Górecka[1], Urbano Díaz[2] and Lucjan Chmielarz[1]

[1]Jagiellonian University, Poland, [2]Universitat Politècnica de València, Spain

36 ***Montmorillonites Intercalated With SiO2–Al2O3, SiO2–TiO2 and SiO2–ZrO2 Pillars in the Role OffEffective Catalysts for Methanol and Ethanol Dehydration***
Małgorzata Rutkowska[1], Andrzej Kowalczyk[1], Monika Skoczek[1], Barbara Gil[1], Piotr Natkański[1], Monika Motak[2], Radosław Dębek[2], Janusz Ryczkowski[3] and Lucjan Chmielarz[1]

[1]Jagiellonian University, Poland, [2]AGH University of Science and Technology, Poland,
[3] Maria Curie Skłodowska University, Poland

37 ***Copper-based Mesoporous Silicas for SOx Trapping Applications: Evolution of the Adsorbent Properties Over Cycling Experiments***
Marc Berger[1,2], Sophie Dorge[1], Habiba Nouali[1], David Habermacher[1], Emmanuel Fiani[2], Matthieu Vierling[3], Michel Molière[4], Jean-François Brilhac[1] and Joël Patarin[1]

[1]Université de Haute-Alsace, France, [2]ADEME,France, [3]GE Energy, France, [4]Laboratoire LERMPS, France

38 ***Design and Synthesis of Stimuli Responsive Nanoporous Silica Supports for Controlled Drug Delivery***
Vladimír Zeleňák[1], Eva Beň ová[1], Miroslav Almáš i[1], Adriána Zeleň áková[1] and Virginie Hornebecq[2]

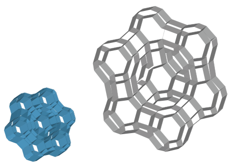
[1]Pavol Jozef Safarik University Kosice, Slovakia, [2]Aix Marseille University, France

39 ***Doping SBA-15 with Nickel Oxide by Freeze-Drying Impregnation***
Gerhard H. Findenegg, Albert Prause, Jens Meissner and Reinhard Schomäcker

Technical University of Berlin, Germany

40 ***Synthesis and Characterization of Physisorption Properties of Novel Core-Shell Systems with Nanoporous Organosilica Shell and Varying Core Materials***
Mandy Jahns[1], Dawid P. Warwas[1], Alexander Mohmeyer[1], Sandra König[2], Michael Fröba[2] and Peter Behrens[1]

[1]Leibniz University Hannover, Germany, [2]University Hamburg. Germany



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Advanced Materials: Oxidic

41 ***Nanoporous Nanoparticles in Drug Delivery: Influence of Release Conditions on Physisorption Properties***
Mandy Jahns, Dawid P. Warwas and Peter Behrens

Leibniz University Hannover, Germany

42 ***Template-Free Synthesis and Characterization of Mesoporous Organosilicas***
Quanchang Li, David Calabro, Ivy Johnson, Mobae Afeworki, Kanmi Mao, Simon Weston, Peter Ravikovitch and Meghan Kochersperger

Exxon Mobil Research and Engineering Company, United States,

43 ***Reactivity of HD and its Simulants with Mesoporous Ceria Nanoparticles Functionalized with H2O2 Ligands***
John Landers[1], Jason Navin[1], Gregory Mogilevsky[2], Trent Tovar, Erik Emmons[1], Ashish Tripathi[1] and Christopher J. Karwacki[1],

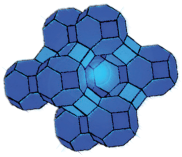
[1]Edgewood Chemical & Biochemical Center, United States, [2]Leidos, Inc., Gunpowder, MD

44 ***Formation of Mesoporosity within Crystalline Metal-Oxide Nano-Crystals by Hydrogen Peroxide Treatment***
Jonathan Colón-Ortiz[1], Shiva Murali[1], Dmitriy Ruckodanov[1], John M. Landers[2] and Alexander V. Neimark[1],

[1]Rutgers University, United States, [2] Edgewood Chemical Biological Center, United States,

45 ***Template-free Synthesis and Structural Evolution of Discrete Hydroxycancrinite Zeolite Nanorods from High-Concentration Hydrogels***
Shaojiang Chen[1], Lukas P. Sorge[2] and Dong-Kyun Seo[1]

[1]Arizona State University, United States, [2]Johannes Gutenberg-Universität Mainz, Germany,



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Advanced Materials: Carbons

46 ***Adsorption of Acetaminophen on Activated Carbons from Cashew Nut Shells***
Svetlana Bashkova and Alexandra Geczo

Fairleigh Dickinson University, Unites States

47 ***Acetaminophen and Salicylic Acid Adsorption on Chemically Modified Activated Carbons: Effect of the Ionic Strength on the Adsorption Thermodynamic Functions***
Juan Carlos Moreno-Piraján[2], Valentina Bernal[1], and Liliana Giraldo[1]

[1]Universidad Nacional de Colombia, [1]Universidad de los Andes, Colombia

48 ***Photocatalysis with Activated Carbon Prepared by Phosphoric Acid Activation of Palm Kernel Shell: Porosity Effect***
Yesid Murillo-Acevedo[1], Juan Carlos Moreno-Piraján[1] and Liliana Giraldo Gutíerrez[2]

[1]Universidad de los Andes, Colombia, [2]Universidad Nacional de Colombia

49 ***Adsorption and Immersion Enthalpy Study of Benzene, Cyclohexane and Hexane on Modified Activated Carbons***
Diana Hernandez Monje[1], Liliana Giraldo Gutiérrez[1] and Juan Carlos Moreno[2]

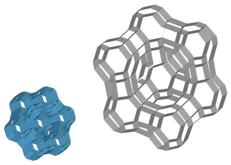
[1]Universidad Nacional de Colombia, Colombia, [2]Universidad de los Andes, Colombia

50 ***Pore Size Effects on Partial Breaking of Coulombic Ordering Structure of Ionic Liquids in Carbon Nanopores***
Ryusuke Futamura[1], Taku Liyama[1], Yury Gogotsi[1,2], Mark J. Biggs[3,6], Mathieu Salanne[4], Patrice Simon[1,5] and Katsumi Kaneko[1]

[1]Shinshu University, Japan [2]Drexel University, United States, [3]Loughborough University, United Kingdom
[4]Sorbonne Universités, France, [5]Université Paul Sabatier, [6]The University of Adelaide, Australia

51 ***Preparation of Low-Cost Activated Carbons from Bio-Waste for Quantum Sieving Applications***
Jaewoo Park, Minji Jung and Hyunchul Oh

Geyongnam National University of Science and Technology, Korea



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Advanced Materials: Carbons

52 ***Heteroatoms-Decorated Hierarchical Porous Carbons Derived from Biomass for Propane Dehydrogenation***
Zhong-Pan Hu and Zhong-Yong Yuan

Nankai University, China

53 ***Boron-Doped Microporous Activated Carbon with Enlarged Surface Area for Efficient Oxygen Reduction and CO2 Capture***
Zhong-Yong Yuan and Jin-Tao Ren

Nankai University, China

54 ***Surface and Interface Engineering of Heteroatoms-Doped Porous Carbon Materials for Efficient Electrocatalytic Processes***
Zhong-Yong Yuan and Jin-Tao Ren

Nankai University, China

55 ***Modified Red Mud with Hierarchical Meso-/Macroporous Structure for Efficient Oxidative Desulfurization Reaction***
Zhong-Pan Hu and Zhong-Yong Yuan

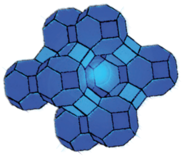
Nankai University, China

56 ***Nanocarbons as Metal-Free Catalysts for Propane Dehydrogenation Reaction***
Zhong-Pan Hu and Zhong-Yong Yuan

Nankai University, China

57 ***Curious Behavior of Polymer of Intrinsic Microporosity / Activated Carbon Composites for Hydrogen Storage Applications***
Katarzyna Polak-Krasna, Sébastien Rochat, Mi Tian, Timothy Mays, Andrew Burrows and Chris Bowen

University of Bath, United Kingdom



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Advanced Materials: Other

58 ***Design and Characterization of Layered Solid from the Intercalation of Organic Molecules Into Transition Metal Nitroprussides***

Yosuan Avila García[1], Ana A. Lemus-Santana [1], Edilso Reguera Ruiz [1] and Osiry Hernández Silva[2]

[1]Centro de Investigación en Ciencia Aplicada y Tecnología de Avanzada, IPN, Mexico,
[2]Insituto Politecnico Nacional, Mexico

59 ***Unusually Strong Dipole-Dipole and Dipole-Quadrupole Interactions in (VO)3[M(CN)6]2·nH2O with M = Fe, Co***

Ana Lemus-Santana[1], Osiry Hernandez[1], Neil Torres[1], Alejandro Rodriguez[1], Lorena Martinez[1] and Edilso Reguera[1]

[1]Instituto Politecnico Nacional, Mexico, [2]CONACyT- Instituto Politécnico Nacional

60 ***Various Cationic ((Sr2+, K+, Fe3+, Ni2+, Cu2+, Zn2+, Mg2+, and Li+)) Exchanged Clinoptilolite As a Adsorbent for CH4/N2 Separation***

Jihong Sun, Shenlai Peng, Shiyang Bai, Teng Ouyang[1] and Xia Wu

Beijing University of Technology, China

61 ***Simple and Competitive Adsorption Study of Nickel (II) and Chromium (III) on the Surface of the Brown Algae D. Antarctica Biomass.***

Jhonatan Ricardo Guarin Romero[1], Jenny P. Rodriguez[1], Juan C. Moreno[1] and Liliana Giraldo[2]

[1]Universidad de los Andes, Colombia, [2]Universidad Nacional de Colombia, Colombia

62 ***Characterization of Converter Sludge as Sorbent and Utilization for Mine Water Cleaning***

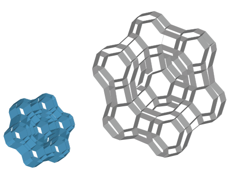
Lucia Rozumová, Jana Seidlerová and Pavel Kůs

Technical University of Ostrava, Czech Republic

63 ***Development of Structured Porous Adsorbents Using 3D Printing Technique for CO2 Capture***

Harshul Thakkar, Ali Rownaghi and Fateme Rezeai

Missouri University of Science and Technology, United States



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Advanced Materials: MOFs

64 ***Enhancing Van der Waals Interactions of Functionalized UiO-66 with Oxygen and Other Non-Polar Gases Via Electron Donation to the Metal-Organic Framework Linker***
Trenton M. Tovar [1], Ivan Lordanov[1], Dorina F. Sava Gallis[2], and Jared B. DeCoste[2]

[1]Edgewood Chemical Biological Center, U.S. Army Research, United States,
[2]Sandia National Laboratories, United States

65 ***Novel Threshold Sensing Architectures Based on Switchable MOF Composites***
Irena Senkovska, Pascal Freund and Stefan Kaskel

Technische Universität Dresden, Germany

66 ***Dualistic Adsorption Behavior of Switchable Pillar Layered Metal-Organic Framework DUT-8***
Irena Senkovska, Volodymyr Bon, Negar Kavoosi and Stefan Kaskel

Technische Universität Dresden, Germany

67 ***Negative Gas Adsorption in Mesoporous Switchable Metal-Organic Frameworks***
Simon Krause[1], Volodymyr Bon[1], Irena Senkovska[1] , Daniel M. Többens[2] , Dirk Wallacher[2], Guillaume Maurin[3] , Franç ois-Xavier Coudert[4] and Stefan Kaskel[1]

[1]Dresden University of Technology, Germany, [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany
[3]Université Montpellier, France, [4]Chimie ParisTech, France

68 ***A Novel Two-Dimensional Zr-based MOF with Photoreactive Surface and its Different Physisorption Behaviour Through Postsynthetic Modification***
Alexander Mohmeyer, Andreas Schaate, J. Rode, Malte Schäfer, Rolf J. Haug, Andreas M. Schneider and Peter Behrens

Leibniz Universität Hannover, Germany

69 ***Controlled Formation of Hierarchical Metal–Organic Frameworks Using CO2-Expanded Solvent Systems***
Huan Doan

University of Bristol, Great Britain

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Advanced Materials: MOFs

70 ***Understanding of the Gate-Opening Effect in Hydrophilic-Hydrophobic Metal-Organic Framework STAM-1***

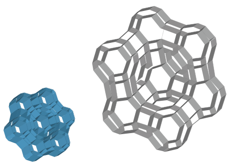
Andrzej Sławek[1], José Manuel Vicent-Luna[2], Bartosz Marszałek[1], Baraba Gil[1], Wacław Makowski[1] and Sofia Calero[2]

[1]Jagiellonian University, Poland, [2]Universidad Pablo de Olavide, Spain

71 ***MOFs for Magnetic Refrigeration: Investigation of Magnetocaloric Effect in MOF-76(Gd)***

Adriana Zelenakova, Vladimir Zelenak, Miroslav Almasi, Pavol Hrubovcak and Ondrej Kapusta

Pavol Jozef Safarik University Kosice, Slovakia



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Experimental Methods

72 ***Effect of Shaping MOFs on Adsorption Performance by Using Adsorption Microcalorimetry***
Sandrine Bourrelly[1], Nicolas Chanut[1], Paul Iacomi[1], Andrew D. Wiersum[1], C. Serre[2], J.-S. Chang[3] and P. L. Llewellyn[1]

[1]Aix-Marseille University - CNRS, France, [2]Université de Versailles St. Quentin, France, [3]Korea Research Institute of Chemical Technology, Korea

73 ***Immersion Calorimetry as a Powerful Tool for the Characterization of MOFs***
Joaquin Silvestre Albero[1], Manuel Martínez-Escandell[1] and Carlos Cuadrado-Collados[2]

[1]University of Alicante, Spain,

74 ***Reference High Pressure CO2 Adsorption Isotherm for Ammonium ZSM-5 Zeolite: Results of an Interlaboratory Test***
Huong Giang Nguyen[1]**,** Laura Espinal[1], Roger van Zee[1], Matthias Thommes[2] and Blaza Toman[1]

[1]National Institute of Standards and Technology, United States, [2]Quantachrome Instruments, United States

75 ***Adsorption of Methane on Zeolite Y: An Interlaboratory Study***
Roger van Zee[1], H.G.T. Nguyen[1], L. Espinal[1] and M. Thommes[1,2]

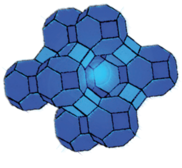
[1]National Institute of Standards and Technology, United States, [2]Quantachrome Instruments, United States

76 ***Dynamic and Static Adsorption of Carbon Molecular Sieves***
Leidy Eugenia Pena Duque and William Betz

MilliporeSigma, United States

77 ***Isosteric Heat: Comparative Study between Clausius-Clapeyron, CSK and Cal-Ad Methods***
Juan Carlos Moreno-Piraján[1], Paola Rodriguez[1], Marlon José Bastidas-Barranco[2], Carlos Arturo Robledo Julio[2] and Liliana Giraldo[3]

[1]Universidad de los Andes, Colombia, [2]Universidad de la Guajira, Colombia, [3]Universidad Nacional de Colombia, Colombia



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Experimental Methods

78 ***Low-Temperature Dynamic Quantum Molecular Sieving of Oxygen Isotopes Using Nanoporous Materials***

Sanjeev Kumar[1] , Katsumi Kaneko[1], Ryusuke Futamura[1], Masahiko Matsukata[2] and Yury Gogotsi[3]

[1]Shinshu University, Japan, [2]Waseda University, Japan, [3]Drexel University, United States

79 ***In-depth Investigation of the Closed Porosity of Glassy Carbons by Scattering Techniques***

Felix Badaczewski[1], Marc Loeh[1] , Torben Pfaff[1] , Bernd Smarsly[1] , Dirk Wallacher[2] and Daniel Clemens[2]

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80 ***Following Adsorption of Water and Hydrogen in Porous Materials–Formation of Hydrogen Bonds and Cooperative Effects***

Margarita Russina and Veronika Grzimek

Helmholtz Zentrum Berlin, Germany

81 ***Cycling Experiments in Microporous Carbon Adsorbed Natural Gas Tanks***

Peter Pfeifer[1], M. Prosniewski[1] and J. Romanos[2]

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82 ***Control of Mechanical Stability of Hollow Silica Particles, and Its Measurement by Mercury Intrusion Porosimetry***

Alan M. Allgeier [1], Jelena Lasio[2], Christopher D. Chen[3], Francis J. Woerner[2] and J. David Londono[3]

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83 ***Pore-Scale Ink Flow in Thin Coating Layer of Paper***

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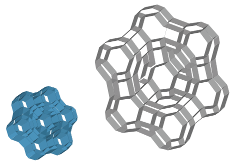

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Experimental Methods

84 ***Digital Rock Physics: Segmentation Comparison for a Carbonate Rock***
Mohamed Sassi[1], A. Islam[1] , T. Faisal[1] and M. S. Jouini[2]

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85 ***Mineralogical Alterations in Calcite Powder Flooded with MgCl2 to Study Enhanced Oil Recovery (EOR) Mechanisms at Pore Scale***
Mona Minde, Reidar Korsnes, Nina Egeland, Merete Madland and Udo Zimmermann

University of Stavanger, Norway

86 ***Nanoparticle Separation on Polymer-Grafted Porous Substrates***
Kolattukudy P. Santo[1], Aleksey Vishnyakov[1], Yefim Brun[2] and Alexander V. Neimark[1]

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Oskar Paris[2], Christian Balzer[1] and Gudrun Reichenauer[1]

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Lukas Ludescher[1,2], Roland Morak[1] , Christian Balzer[3] , Stefan Braxmeier[3] , Florian Putz[4] , Michael Elsässer[4] ,
Gudrun Reichenauer[3] , Nicola Hüsing[4] , Oskar Paris[1] and Gennady Y. Gor[2]

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89 ***Multifaceted Experimental Study of Molecular Diffusion and Transport through Nanoporous Alumina***
André Morgado Lopes[1], Véronique Wernert[1], Loïc Sorbier[2], Vincent Lecocq[2] and Renaud Denoye[1]

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90 ***Active Behavior of Graphene Nanowindow Rims***
Fernando Vallejos-Burgos and Katsumi Kaneko

Shinshu University, Japan

91 ***Determination of gas diffusivity in alumina porous materials using Flux Response Technology***
Hai P. NGUYEN[1], Fessehaye W. Zemichael[2], Satoru Kato[3], Satoshi Nagao[4] and Klaus Hellgardt[2]

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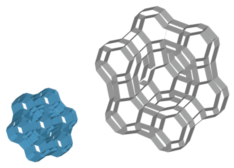

CPM8 | INVITED LECTURES
SUNDAY, MAY 6, 2018

Nanoconfinement Mediated Materials/Adsorption Engineering

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It is well-known that confinement of atoms, molecules, and ions in nanoscale pore spaces induce unusual effect. In particular, confinement in nanoscale graphitic pores has provided explicit confinement effect, because the graphitic wall has no specific sites and offers the greatest van der Waals attractive force filed per weight. One representative effect is so called superhigh pressure effect, which was evidenced in enhanced dimerization of NO molecules in carbon nanopore in 1987[1] by author's group. Later this enhanced NO dimerization was confirmed in single wall carbon nanotubes by Yates et al [2]. Gubbins et al has continuously studied this effect theoretically, showing the statistical view on the superhigh pressure effect[3]. This paper describes new progress in this superhigh pressure effect such as high pressure phase transition of KI[4] and S[5]. The superhigh pressure effect can be applicable to high pressure organic synthesis without an autoclave [6], which will be shown.

Recently we found a quite unique confinement effect for ions inherent to electrical conductive nature of nanoporous carbons. We evidenced that when ions were adsorbed in carbon nanoscale pores, electrons in carbon walls moved to compensate the repulsive situation between co-ions to form co-ion pairs[7]. The highly confined situation is quite effective for isotope separation even such as ${}^{18}O_2$-${}^{16}O_2$ mixed gas, which will be presented [8].

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Properties of Water confined in Periodic Mesoporous Organosilicas: Nanoimprinting the local structure

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The confinement of liquids in porous media greatly influences their physical properties, in particular, when the pore size approaches the molecular length scale. Several mechanisms, such as the pure geometrical restriction and the liquid-solid interaction at the interface contribute to the confinement effects, however, their roles for the drastic changes in the thermodynamic and dynamic behaviors of the liquids are not clearly understood. Especially, water molecules adsorbed on the surface and restricted within the pores are interesting in the scope of biochemistry, catalysis, and energy storage. The influence of the pore size on the melting and freezing points of confined water has been studied extensively. It is known that the properties of water in confined spaces with extents of a few nanometers will be altered and that for example the freezing/melting point can be shifted to temperatures below 220 K or completely suppressed [1]. In contrast, fewer studies have been made concerning the effects of the surface polarity on the properties of spatially confined water, which may be due to the lack of highly defined porous substances.

Periodic mesoporous organosilicas (PMOs) fill this gap perfectly because they combine the highly ordered pore structure of the well-established M41S-phases with the variety of surface chemistry within the pores. PMOs are synthesized using bis-silylated precursors of the form $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ where R is an organic bridging group which can be altered according to the desired surface properties [2,3]. Furthermore, PMOs with an aromatic bridging group may exhibit a molecular-scale periodicity within the pore walls. This allows a periodically alternating surface chemistry along the pore channel, caused by arrays of silica and aromatic organic groups. It is assumed that water will adsorb differently at the diverse areas of the pore wall surfaces owing to the varying hydrophilic or hydrophobic properties. Because of the endless possibilities for the organic bridging function, the surface chemistry of PMOs can be fine-tuned.

Here, we show that the molecular mobility of water confined in periodic mesoporous organosilicas (PMOs) is influenced by the polarity of the organic moiety. Multidimensional solid-state NMR spectroscopy directly probes the spatial arrangement of water inside the pores, showing that water interacts either with only the silicate layer or with both silicate and organic layers depending on the alternating surface polarity. A modulated and a uniform pore filling mode are proposed for different types of PMOs [4]. Our study gives a molecular-level picture of the adsorbate-surface interaction, which helps understanding various confinement effects and provides a new design concept of the pore structures with the desired properties.

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Density of adsorbed hydrogen at low temperatures in mesoporous materials

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Hydrogen storage by physisorption in porous materials has gained considerable interest in the past years since many novel materials have been developed possessing ultra-high porosity. Typically, the storage capacity is characterized at high pressures and liquid N_2 temperatures. Additionally, the specific surface area is characterized by nitrogen adsorption and a linear correlation between the hydrogen uptake and the BET area is found (Chahine´s Rule). The aim of this study is to characterize porous materials by one measurement, i.e. a low–temperature and low-pressure isotherms of H_2 at 20 K [1,2]. The prerequisite for this approach is the exact knowledge of the density of the adsorbed H_2 layer. A mesoporous silica KIT-6, which possesses a well-defined pore size and no microporosity, was used as reference material. Using cryoadsorption experiments with four different gases (H_2, D_2, Ar, N_2) at their condensation temperature, respectively, we calculated the molecular areas for adsorbed H_2 and D_2 and the density of the BET monolayer. Under the assumption that a monolayer is formed, the evaluation of the isotherm yields to a density of adsorbed hydrogen (202 kg/m^3), which is three times higher than its bulk-liquid density (71 kg/m^3) and exceeds more than two times the solid hydrogen density (89 kg/m^3). In order to gain additional insight, we performed a systematic study using Inelastic Neutron Scattering (INS) at the vibrational spectrometer VISION at SNS, ORNL (Spallation Neutron Source, Oak Ridge National Laboratory). The normalized neutron intensity as a function of its energy and the relative intensities of the spectral peaks allow us to directly follow the formation of the adsorbed layer. The hydrogen adsorption isotherms are correlated to the INS vibrational spectroscopy experiments measured for different gas loadings and temperatures. The H_2 density in a hexagonal 2D lattice is calculated for different dimmer orientations.

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Phase transitions in geometrically disordered mesoporous solids

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Despite a notable progress attained in the understanding of phase behavior of fluids in mesoporous materials with ordered pore systems, many aspects of these phenomena occurring in disordered porous solids still remain not fully explored. For a collection of isolated single-pores, the general adsorption isotherm (GAI) equation [1] correlates the phase state in the individual pores, as described by the respective kernels, with the experimentally measured isotherm. If these individual pores are brought into direct contact with each other, the phase states in two adjacent pores may become interdependent, leading to the emergence of cooperativities in the corresponding phase transitions. Under these conditions, the applicability of GAI may not always be justified. In the present work we consider linear chains of interconnected single cylindrical pores with different pore diameters [2]. The pore sizes of two adjacent pore sections are considered to be statistically uncorrelated. For this pore space architecture and for large ensembles of such linear chains we derive rigorously an analogue of the GAI equation, which takes explicit account of the statistical correlations between the phase states in two adjacent pores [2]. The emergency of these correlations occurs naturally by considering the families of the conventional kernels for adsorption and desorption in open-end cylindrical pores complemented with two more kernels obtained using closed pores (to model the occurrence of the cavitation phenomenon) and using capped cylindrical pores (to model elimination of metastability along the adsorption branch). To validate the framework developed, we have performed simulation studies (GSMC and lattice gas MFT) of the respective geometric models and have found excellent agreement between the predictions of the theoretical isotherm equation and the simulation results for the boundary sorption curves, for the adsorption and desorption scanning curves, and for the scanning loops. The phase behavior predicted by this model reproduces the majority of experimental observations reported in the literature and thus provides an efficient approach to uncover physical mechanisms behind these observations. Notably, this framework is generally applicable for any phase transitions including condensation/evaporation, freezing/melting, and also for other phenomena exhibiting pore-size dependent behavior, such as mercury intrusion/extrusion.

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Probing interfacial water dynamics in colloidal and nanoporous systems by Nuclear Magnetic Relaxation Dispersion.

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The confined dynamics of water molecules near a colloidal surface or inside a pore is an intermittence of adsorption steps near the interface with the possibility of a surface diffusion and excursions in the pore network [1,2]. Depending of the strength of the interaction in the layer(s) close to the surface and the dynamical confinement of the distal bulk liquid, the exchange dynamics can be more or less fast. The average time spend in the surface proximal region (also called the adsorption layer) between a first entry and a consecutive exit allows to estimate the level of nanowettablity of water.

The Nuclear Magnetic Relaxation Dispersion (NMRD) is an affective experimental method to follow the intermittent molecular dynamics near an interface [2,3]. NMRD allows to analyze this dynamics in the time frequency domain and provide dynamical information inside a temporal window between ns and some microseconds. This time window is complementary to other more traditional spectroscopies such as QUENS, Pulsed field gradient NMR technics.

In this conference, we discuss various experimental and theoretical studies of the intermittent dynamics using NMRD. Two groups of interfacial systems will be analyzed: first, suspensions of colloidal clay particles or macro porous systems exhibiting a relatively weak bulk confinement but variable surface interactions [4]; second, nanometer scale pore networks where excursion of the confined fluid is restricted.

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New SAPO-Based Nanoporous Materials and Some Potential Applications

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Our recent efforts in nanoporous materials synthesis have yielded several SAPO-based framework topologies with small nanopores and unprecedented structures. These new structures are in the ABC-6 family, which will be described in this presentation. Additionally, unique adsorption properties reveal potential applications in adsorption heat pumps as well as in applications in catalysis. Aspects of these potential applications, including preparation and attempts to understand and improve heat transfer properties of thin adsorbent zeolite sheets for application in adsorption heat pumps, will also be outlined in this presentation.

Porosimetry: Applications and Challenges in Fluid Catalytic Cracking

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Fluid catalytic cracking (FCC) is the major technology used by petroleum refineries to convert distilled crude oil into transportation fuels and other petroleum based products. W. R. Grace is the leading supplier of FCC catalysts as well as FCC additives used to reduce harmful emissions from refineries. The development and advancement of current FCC technologies relies heavily on understanding the catalyst's physical and chemical properties. The catalytic performance is greatly affected by surface area and pore structure, which is dictated by the raw material properties (zeolite, clay, silica, alumina, etc) and manufacturing process. This presentation will cover the different porosimetry techniques used in FCC as well as the needs/challenges in characterizing the FCC catalyst pore structure.

From molecular sieves to industrial catalysts: the past, present and future in Total

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Heterogeneous catalysis is an important field of expertise for Total, with some 90% of refining and 100 % of base chemicals processes involving catalysts in at least one of their steps. A new long-lasting energy transition makes catalysis even more important than before. This is greatly due to availability of cheap cleaner feedstock like natural gas and the emergence of alternative, renewable sources of energy. At present, because of complex interplays between technology, political regulations, societal needs and consumer attitudes, innovation in catalysis remains amongst the cheapest and most efficient solutions for Total. Total has been always active in research in catalysis, and this review present some recent success stories of commercialization of molecular sieves-based catalyst for addressing major challenges.

Alcohols represent an advantageous and easily transportable feedstock for future supply in chemicals. These molecules can be synthesized from biomass and CO_2 utilizing renewable power, as well as from (bio)-methane. Molecular sieves play an important role in the alcohol transformation. A comparison of the zeolitic routes versus non-zeolitic ones will be discussed. One of the important transformations is synthesis of propylene from alcohol, and there remains a significant room for optimization of the yield of this process.

Recent years have witnessed introduction of many advanced tools, which allow characterization and accelerating testing of catalysts with previously unattainable resolution and sensitivity. They have revealed that molecular sieves are more heterogeneous than one may think. New computational tools and structure – performances analytics are much easily accessible and more and more frequently used for results prediction in Total. We will also figure out how the latest developments help to understand and resolve the mechanistic paradox. Application of ferrierite (FER) in a selective skeletal isomerization of n-butenes to isobutene and transformation of iBuOH to n-butenes will be discussed. Surprisingly, the same type of structure catalyzes the reverse reaction with alcohols versus olefins [1]. While the dehydration reaction on this intermediate pore zeolite appears simple on paper, it follows, in fact, a rather complex reaction pathway. While the role of the carbonaceous deposits on the butenes formation still needs to be better understood, it is evident that pore mouth catalysis and coke deposition play a fundamental role in the transformation. A hydrocarbon-pool mechanism is proposed to account for these observations.

Although the progress within industrially relevant characterization tools had been expected, very few predicted a tremendous progress in zeolite synthesis, emergence of so many new applications for zeolites as well as creation of so many innovative zeolite-based materials like nanolayers, hierarchical, 3D printed, composites, albeit still searching for relevant markets.

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Kerogen-Hosted Porosity: Controls on Storage and Transport in Gas Shale

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Oil and gas production from shales have revolutionized the energy industry in recently years. As opposed to the sandstone and carbonate rocks that comprise reservoirs for conventional petroleum production, unconventional shales are characterized by very low porosities and permeabilities. Moreover, much of the hydrocarbon-saturated porosity is hosted not by mineral grains (as is the case for conventional reservoirs) but in a disordered organic solid called kerogen (kerogen is defined as organic matter in sedimentary rock that is insoluble in any organic solvent).

Here we will review current understanding regarding the structure of kerogen, including both chemical structure assessed by various spectroscopies and pore structure assessed by various microstructural analyses. We will also review models of hydrocarbon transport through kerogen-hosted porosity, including attempts to assess the impacts of kerogen structure on hydrocarbon production. Finally, we will present challenges faced by the industry in characterizing the structure of kerogen.

Water-based route towards dispersed CuO-loaded catalysts: texture, structure and catalytic performance in automotive exhaust gas conversion

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In the early 1970s, the first precious metals loaded catalyst based on Pt and Pd was manufactured and since then, scientists have been continuously improving the design and the composition of the automotive catalyst with the aim to create a more durable, active and poison-resistant catalyst. Through the evolution of the vehicle catalytic converter however, its substantial active elements have not been significantly changed: in the current three-way catalyst (TWC), platinum group metals (PGMs) Pt, Pd, Rh have been applied for the reduction of hydrocarbons, carbon monoxide and NO_x. Despite their effectiveness for emission gases control, the rising issue is the scarcity and consequently also the high cost of this type of materials. Within this context, transition metal based catalysts, for instance Cu, are a potential candidate to replace Pt and Pd for catalytic oxidation reactions. However, its major drawback is the low intrinsic activity and stability. Hence, developing a well-dispersed and industrial up-scalable catalyst preparation method becomes a necessity in order to mitigate the above mentioned obstacles.

Here, we present a cost-efficient, optimized water-based dispersion method for CuO-loaded catalyst preparation. By utilizing the interplay between the steric hindering effect of copper tetra-ammonia and electrostatic adsorption of copper complexes on suitable supports (CuO/γ-Al_2O_3, CuO/SBA-15), an excellent CuO-nanoparticles dispersion can be realized. It will be shown that the prepared CuO-catalysts exhibit a uniform dispersion of small CuO particles on the support's surface. The catalysts are characterized by a wide variety of techniques, such as N_2-sorption (porosity), UV-VIS-DR, SEM, XRD, N_2O titration, H_2-TPR and XPS (for determination of the CuO dispersion). The influence of the structural and textural properties of the support material, and the loading and the dispersion of the CuO-species (in relation to the preparation conditions) will be discussed. Moreover, the catalytic results of the different catalysts, together with the outcomes of the classical PGMs TWC as benchmark will be presented (for CO, CH_4, hydrocarbons, NO conversion). It is shown that the optimized water-based synthesis method applied here leads to very effective dispersed CuO-based catalysts with an outstanding CO and hydrocarbons conversion, comparable to the commercial precious metal loaded automotive catalysts.

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Characterizing the Mass Transfer Kinetic Mechanism in Microporous Adsorbents Using the Volumetric Technique

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We present a methodology to represent kinetic data from volumetric systems that allows to distinguish clearly between internal diffusion and surface resistances when studying the kinetics of adsorption on commercial pellets of microporous materials.

For fast adsorption kinetics, the traditional method of converting the pressure signal of the dosing cell into an uptake curve and then plotting this vs the square root of time is not easily applicable because of the initial effect of the flow through the valve between the dosing and uptake cells. The new approach we propose is based on a semi-log plot of the reduced pressure in the dosing cell vs time, and provided that the volumetric experiment is carried out under isothermal and linear conditions, a simple inspection of this plot reveals clearly which process is prevailing. A detailed analysis of the models indicates also that the long-time asymptotic decay is very sensitive to the mass transport mechanism, because the equilibrium properties are fully defined by the initial and final state of the system.

The methodology will be demonstrated on commercial adsorbents used in air separation. To discuss both limiting behaviours experimental results will be presented on zeolite LiLSX beads which are macropore diffusion controlled and on carbon molecular sieve (CMS) beads which exhibit primarily a surface resistance. In the case of the CMS sample we will show that the response allows also to characterize the distribution of surface barriers present in the material. This distribution can only be obtained from kinetic experiments and we will show how this important property can be obtained from volumetric measurements.

CPM8 | INVITED LECTURES
MONDAY, MAY 7, 2018

Structural Characterization of Complex Fluids in Tubular Nanopores

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Ordered mesoporous silica materials have outstanding properties for applications in gas storage, separation processes, and catalysis. Due to the uniform size of their primary pores, and the ability to tailor the size, shape and surface chemistry of the pores, these materials have also potential for applications in the biomedical field, including the immobilization and controlled release of proteins. However, a structural characterization of complex fluids and soft matter confined in porous substrates still forms a major challenge. Small-angle neutron scattering and diffraction (SANS and SAND) are useful tools for such studies, as they allow to highlight different aspects of the structure by contrast variation.

Small-angle scattering from complex fluids confined in the pores of periodic mesoporous materials generally represents a sum of two contributions: Bragg scattering (diffraction) from the pore lattice and diffuse scattering from the nanoscale entities in the pores [1-3]. Analysis of the diffuse scattering contribution provides information about the mean separation of these entities in the matrix. Bragg scattering can also be affected by adsorption in the pores via a modulation of the form factor, which allows to distinguish, for example, between discrete nanoscale objects or a uniform adsorbed layer at the pore wall. This information is extracted from the change of intensity of the Bragg peaks as a function of the concentration of the adsorbate.

In this contribution some recent studies of complex fluids in SBA-15 silica will be discussed. This will include a comparison of adsorbate structures of non-ionic and cationic surfactants, the co-assembly of cationic surfactants with proteins, and a structural characterization of microemulsions confined in the pore space.

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Deliquescence of NaCl crystals in confinement

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Deliquescence is the process by which a solid picks up water vapor from the surrounding air and forms a solution. The deliquescence of a bulk salt crystal is characterized by the deliquescence humidity (DRH) of the salt. The DRH also equals the water activity (a_w), i.e. the equilibrium relative humidity, of the saturated salt solution. It has been shown that the DRH of levitated nano-sized NaCl crystals increases as the crystal size decreases [1,2].

In the present work, we have studied the deliquescence of NaCl crystals confined in the pores of mesoporous SBA-15 silicas and porous glass. The materials were impregnated with NaCl solutions avoiding over-filling the available pore volumes. After drying, water vapor sorption isotherms of bulk NaCl, the pure host materials and the porous substrates containing NaCl were determined. The DRH of bulk NaCl is $p/p_0 = 0.75$, i.e. deliquescence occurs at water vapor pressures far below capillary condensation occurs in any of the unloaded substrates. In contrast to levitated NaCl nanocrystals, the DRH of the confined NaCl nanocrystals is significantly lower and decreases with decreasing pore size. Thus, deliquescence causes a significant shift of capillary condensation to lower relative pressures.

A thermodynamic model approach is used to predict the deliquescence of both levitated and confined NaCl nanocrystals. The model includes the influence of crystal size and Laplace pressure on solubility and the influence of the convex and concave vapor–liquid interfaces in the solutions droplets and in the pores filled with a highly concentrated solution, respectively. The calculations agree nicely with the experimental data and reveal that the shift in the DRH is largely the result of the curvature of the vapor–liquid interface. In contrast, the increased solubility of nanocrystals compared to bulk crystals has only a minor effect on the DRH.

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Direct investigation of the adsorbate evolution in mesoporous silicon combining anomalous SAXS, EXAFS and Xenon physisorption

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Gas physisorption in mesoporous materials and the associated capillary hysteresis intrigue the scientific community since decades. These phenomena are largely exploited for the characterization of porous solids, which justify the strong need for their complete understanding. To date, the major hurdle lies in a reliable description of the state of the confined fluid, which is usually given by measuring a macroscopic observable, i.e. the amount of adsorbed gas.

Despite computational methods, *in situ* techniques combining gas physisorption with x-ray scattering methods showed in the last years to be valuable tools to get deeper insights into gas adsorption phenomena [1,2]. Using the contrast variation technique, a more detailed, locally resolved description of the process could be given by the analysis of the scattering signals of the material pore structure. However, clear assessment of the adsorption process was still missing since the adsorbate evolution in the mesoporous host could be only indirectly investigated.

Herein, we present a novel analytical approach, which combines anomalous small-angle x-ray scattering (ASAXS), x-ray absorption spectroscopy (EXAFS) and gas physisorption in a single experiment, enabling direct characterization of the adsorbate phase at different length scales. The research addresses Xenon (Xe) physisorption at its boiling point (T = 165 K) in a mesoporous silicon membrane with 10 nm wide pores. SAXS was performed under anomalous scattering conditions, i.e. at energies near the absorption edge of Xenon ($\lambda_{L\text{-}III} = 4.781$ keV), on different points of the adsorption and desorption branch of the isotherm. Thus, from the resonant scattering curves of Xe the mesoscopic evolution of the adsorbate (multilayer formation, capillary condensation and desorption) could be directly investigated. In addition, the interatomic distances of adsorbed Xe atoms were analyzed by EXAFS at chosen points of the isotherm. At saturation conditions sensitive contraction of the confined fluid was observed with respect to bulk.

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Liquid crystals confined in mesopores: Adsorption isotherms, self-assembly of supermolecular helices and extremely fast electro-optics

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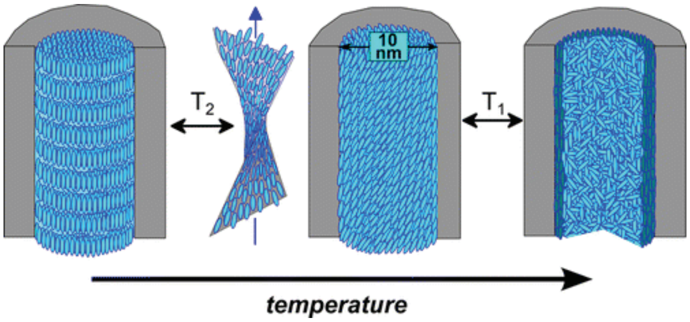

The adsorption, orientational as well as translational order of thermotropic rod-like and discotic liquid crystals confined in silica and anodic aluminium oxide mesopores are explored by high-resolution linear and circular optical birefringence as well as neutron and X-ray diffraction texture analysis. The results are compared to experiments on the bulk systems. For a discotic system in mesoporous silica we find a layer-by-layer formation of circular bent columns. Monte Carlo simulations corroborate the quantized nature of this confined phase transition. For a thermotropic ferroelectric liquid crystal confined in anodic aluminium oxide membranes we observe a thermal-history independent formation of chiral smectic C* helices and a reversible chevron-like layer buckling. A linear electro-optical birefringence effect evidences collective fluctuations in the molecular tilt vector direction along the confined helical superstructures, i.e. the Goldstone phason excitations typical of the para-to-ferroelectric transition. Their relaxation frequencies are studied as a function of pore radii and found to be two orders of magnitude larger than in the bulk, evidencing an exceptionally fast electro-optical functionality of the mesoporous liquid-crystalline nanohybrids.

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Impact of the surface chemistry on the methane hydrate formation in carbon nanopores

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Methane hydrate (MH) is an ice-like compound that is formed when water and methane come into contact under thermodynamically favorable conditions. Enormously amount of natural methane hydrates can be found in deep-water marine environments and in the permafrost, whereas synthetic MHs are postulated as an alternative way to store natural gas by mimicking nature. Unfortunately, storing methane via wet strategy is not an easy task. Several approaches have been tested in order to increase the gas-liquid contact area, and consequently the rate of MH formation. In this context, nanoporous carbon has successfully demonstrated to be an excellent platform able to host and promote the synthesis of MHs [1, 2]. Taking into account that in these systems the methane molecules are trapped in cavities formed by hydrogen-bonded water molecules (sI structure $CH_4{\cdot}5.75H_2O$ when all the cavities are occupied), the presence of a certain surface chemistry able to interact with the water molecules must exert an influence in the MH formation process, either positive or negative. We recently described that the incorporation of oxygen-containing surface groups in petroleum-pitch derived carbon (with a wide pore size distribution) modifies the water activity and water distribution within the carbon sample, the preferential location of oxygen groups at the pore mouth promotes water clustering in larger pores thus promoting the methane hydrate formation at lower pressures (around 3-4 MPa) [3]. In this work, we will report the influence of the surface chemistry on the methane hydrate performance in porous model carbon. Ultrahydrophilic ordered mesoporous carbons and its hydrophobic analogue exhibiting mean pore size of 10 nm were selected, humidified and submitted to increasingly methane pressure to promote the methane hydrate formation. The methane uptake isotherms at different temperatures as well as the kinetics performance were recorded and analyzed.

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Compression and High Pressure Effects In Adsorbed Films

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There is much experimental evidence that the molecules in a fluid or amorphous film adsorbed on a solid substrate can experience strong compression. Such compression has been observed by direct *in situ* experiments; examples include X-ray diffraction[1], low energy electron diffraction[2] and microcalorimetry measurements[3], and in indirect measurements where high pressure phases and reactions occur in such films even when the bulk phase in equilibrium with the film is at low pressure. This compression has also been observed in molecular simulations[4-7] (Fig. 1). Such compression is particularly evident for solid substrates having a high surface atomic density, such as carbons, resulting in strong wetting. Compression can occur in both the *z*-direction, normal to the surface, and in the *xy* plane parallel to the surface. Molecular simulations show that the pressures in such films can be greatly enhanced over that of the bulk fluid phase, and that this enhancement is particularly large in the direction parallel to the surface of the substrate. For example, for an adsorbed film of Lennard-Jones argon molecules on a carbon substrate at 87.3 K (the normal boiling point of argon) and 1 bar bulk pressure, the tangential pressure in the adsorbed layer in contact with the surface is of the order 20,000 bar[5], an enhancement of more than 4 orders of magnitude. Even higher tangential pressures have been predicted to occur when chemisorption or chemical reaction occur in the film.[7]

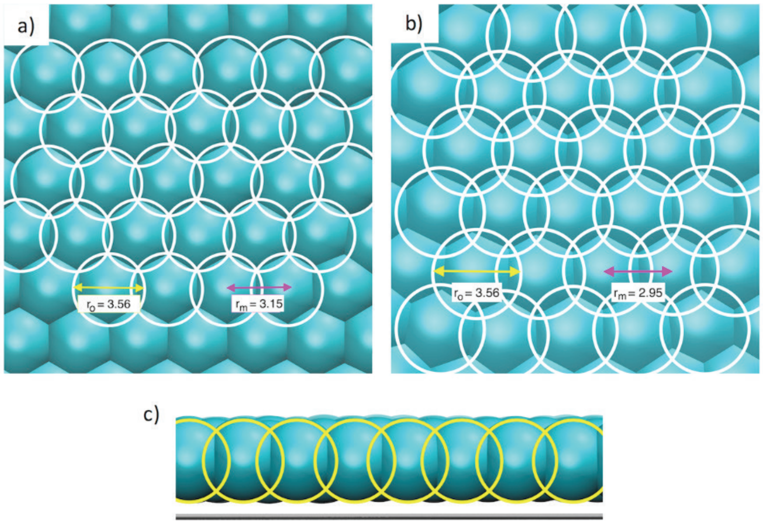

Figure 1. Snapshots of simulations, showing compression of the adsorbed contact layer next to the pore wall in the xy plane for two different values of the wetting parameter: (a) $r_m = 3.15$ Å and (b) $r_m = 2.95$ Å, respectively; c) Side view of lateral compression in the adsorbed layer. Here r_m is the mean distance between molecular centers of neighbors in the film; $r_0 = 3.56$ Å is the separation between neighbors when no compression occurs.[7]

The cause of these high in-film pressures will be discussed, and where possible comparison with experimental results will be made[8]. In general, the pressure is not uniquely defined at the nano-scale in inhomogeneous systems. Several methods to approximately quantify the effective pressures in such inhomogeneous systems will be discussed and compared.

High pressures are required for many processes in the chemical, oil and gas, pharmaceutical and other industries. Examples can be found in many heterogeneous gas reactions, in the production of pharmaceuticals, and in the synthesis of high-pressure solid phases of materials with desired properties, such as semiconducting or superconducting behavior. For some syntheses, pressures of thousands or tens of thousands of bar are necessary to overcome activation barriers. In other applications even higher pressures may be needed, approaching one million bar or more; such pressures can be achieved only in diamond anvil cells for very small samples, and are not practical at present on an industrial scale. Even when possible, achieving such high pressures is very energy-intensive, expensive, and harmful to the environment. At present, industrial processes are mostly limited to relatively low pressures, below about 30 MPa. An alternative approach to the production of high pressures, based on the very strong attractive force fields exerted by some solid substrates, may be possible. Such an approach would not be energy-intensive, environmentally damaging or expensive, and so could lead to promising new technologies. It is mainly limited by our current lack of fundamental understanding of the atomic level processes involved.

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Calculation of the Isosteric Enthalpy of Adsorption in Monte Carlo Molecular Simulation: Consideration of Bulk Phase Nonideality and Isosteres of Total Adsorption

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In engineering applications of adsorption, it is important to consider the heat released by the adsorption process, as the various choices made in managing that heat will have different effects on the overall process. It may represent any or all of 1) the energy cost of controlling column temperature, 2) a change in adsorption equilibrium to lower loading capacity, or 3) the energy cost of desorption during adsorbent regeneration. A differential heat of adsorption, that is the change in molar enthalpy of during transfer of gas to the adsorbed phase, is the usual thermodynamic metric for describing the heat evolved by adsorption. The preferred version of the differential heat is now usually called the isosteric enthalpy of adsorption (IEA), *i.e.*, the heat released by the transfer of gas at fixed adsorbate loading [1]. Whether from experiment or simulation, this quantity may be obtained by isostere analysis of a sequence of isotherms at closely spaced temperatures, via the Clausius-Clapeyron equation. For molecular simulations, this IEA may alternatively be computed from fluctuations of the internal energy and molecule count. Yet, there are competing fluctuation definitions of the IEA, which yield markedly different results [2-4], and controversies regarding which measure of adsorbate loading (absolute, total, or excess) should be held fixed [5-8]. Furthermore, equations for the IEA for multi-component adsorption are underdeveloped compared to their single-component counterparts.

In the present work, we reexamine equations for the IEA in light of recent work [5-8] that stresses the importance of analyzing *absolute adsorption* isotherms during isostere analysis, and accordingly present new fluctuation-based expressions for the IEA for both single- and multi-component adsorption. These expressions account for non-ideality of both the adsorbed and bulk gas phases, regardless of the gas composition. Using flat-histogram sampling in Monte Carlo molecular simulation [9], we apply these equations to both single- and multi-component gas adsorption to show how TMMC can yield the IEA for an entire isotherm from statistics collected in a single simulation. We also demonstrate that these calculations agree with isostere-based calculations from either the formal Clapeyron equation or the Clausius-Clapeyron, depending departure from ideality in the bulk gas phase. Additionally, we present sample calculations that highlight the differences between the various definitions of the IEA and discuss when these differences may prove critically important. Overall, we aim to place simulation-based IEA calculations on a firmer foundation so that this important thermodynamic quantity may be used more confidently for the design and analysis of adsorption processes.

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First Principles Monte Carlo Simulations of Adsorption and Reaction Equilibria

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First principles Monte Carlo simulations, where the energy is calculated on the fly using Kohn-Sham density functional theory, are used to explore (a) the unary and multi-component adsorption of gas molecules in metal-organic frameworks with under-coordinated metal sites, and (b) the influence of nanoscale confinement and preferential adsorption sites on reaction equilibria in cation-exchanged zeolites. The talk will highlight simulation methodologies and microscopic-level origins of the observed thermodynamic behavior.

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Adsorption Model for Porous Oxides with Corrugated Cylindrical Pores. 2D-NLDFT Approach

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In this work we propose using the two dimensional version of the non-local density functional theory (2D-NLDFT) to improve adsorption models (kernels) for the analysis of adsorption data measured on the oxide materials with cylindrical mesopores. The existing standard models for such materials based on the one dimensional (1D) NLDFT assume the smooth energetically uniform surface of the pore walls. The theoretical nitrogen adsorption isotherms calculated for the mesopores with uniform surfaces show typical layering transitions for both slit and cylindrical pores. In the case of slit pores, the layering transitions lead to two well-known artifacts observed in the calculation of the pore size distribution (PSD) of activated carbons: (1) the minimum in the PSD plot at about 10 Å and (2) the typical S-shaped deviation between the theoretical and experimental isotherms. The introduction of a carbon pore walls corrugation and a 2D-NLDFT treatment of the fluid density in the pores led to the elimination of the artifacts and to excellent fit of the model to the experimental data [1-2].

A similar approach is applied here to the 2D-NLDFT model of argon adsorption in cylindrical pores of porous oxides. We find that a geometrical corrugation imposed on the surface along the axis of a cylindrical pore reduces or eliminates the layering transitions of the calculated adsorption isotherms. An example of the new analysis approach is shown in Fig. 1 where we compare the results of the PSD analysis using the standard and the 2D-NLDFT model applied to argon adsorption isotherm measured on the MCM-41 sample [3]. The new model gives a much better fit to the experimental data and the PSD in better agreement with the XRD analysis [3].

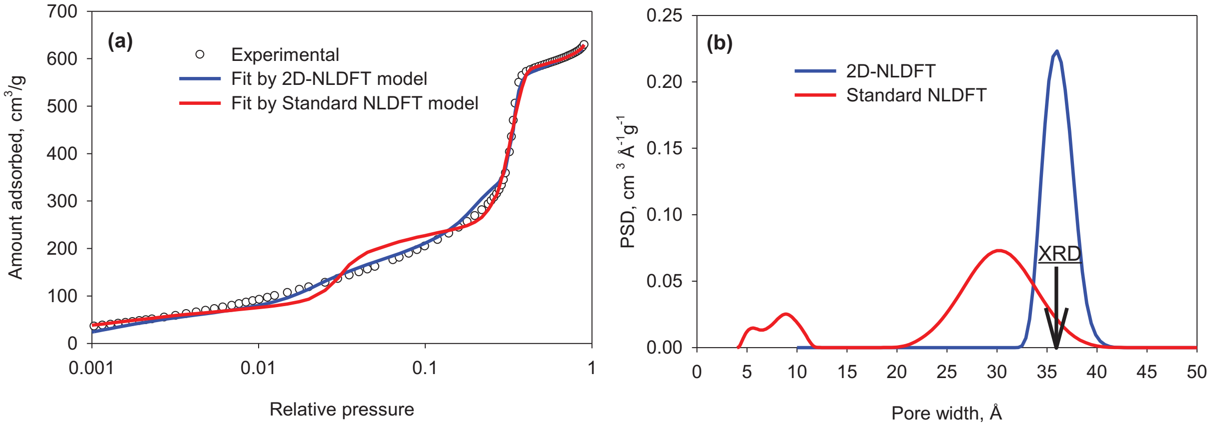

Fig. 1. PSD analysis of MCM-41 (3.6 nm) sample by the standard and 2D-NLDFT models. (a) Fits of the models to experimental Ar isotherm at 87 K. (b) Calculated PSDs.

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Ion Adsorption in Microporous Materials Studied by Classical Density Functional Theory

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The ion adsorptions in porous materials are associated with many engineering applications including water desalination, separation and energy storage. Whereas a large number of microporous materials (pore size less than 2 nm) have been prepared in experiment as functional materials, theoretical model on molecular level allowing for accurately describing the properties of ion adsorption in micropore is still few. The challenge mainly originates from the ill capture of overlapping electrostatic potential and de-solvation effect. Here, by employing rigorous yet generic boundary conditions for the Poisson equation that accounting for the electrostatic contribution, we introduce an extended classical density functional theory (CDFT) which enables us to investigate the ion adsorption in both micropore and mesopore under charging or neutral condition. This theory is first rationalized by comparing the CDFT predictions on local ion concentrations with corresponding simulation results. Afterwards, the capacitances of real porous electrodes are particularly accessed. Taking the TIC-CDC material as case study, we evaluate the capacitance in terms of varying pore size, and then by combining the pore size distribution in porous electrode, the total compactors for different TIC-CDC based electrodes are finally computed, which displaying a satisfactory agreement with the reported experimental measurements. In addition, anomalous capacitances increasing with average pore size is confirmed in microscopic pore. The theoretical model developed in this work provides a promising tool for computational based rational design of microporous materials facing diverse application purpose.

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Nanoporous Biomaterials

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Biomaterials, the materials from which implants, prostheses or tissue engineering scaffolds are made, get into close contact with cells, tissues, and living beings. In addition to restoring the actual function of a body part (e.g. a hip joint, a tooth, a sensory system), the biomaterials must fulfill additional tasks, like enhancing the tissue integration of an implant, fighting implant-associated infections, positively influencing the healing process or directing the formation of a certain tissue. For these purposes, the controlled provision of bioactive agents, liberated from the implant, is a viable route. Mere sorption and release of a bioactive agent from an implant surface is ineffective due to the small amounts of agents that can be stored; polymer implant coatings can only store a limited drug amount (<10-20 mass-%); at higher content the drug molecules act as plasticizers, deteriorating the mechanical properties of the polymer.

Inorganic nanoporous materials, on the other hand, offer a permanent pore system, typically with ca. 50% of the volume being available for drug storage. In many cases, the surface offers reactive OH groups which can be used for the designed chemical modification to increase storage capacity and release behavior, including triggered release processes. The most prominent nanoporous biomaterial is mesoporous (or nanoporous) silica which has mainly been investigated as nanoparticles for combating cancer and other diseases [1]. In these approaches, the nanoparticles are injected into a body liquid and are typically equipped with targeting vectors which should guide them towards the desired place of application. However, doubts have arisen about this principle [2].

In contrast, in our approach we use nanoporous biomaterials as part of an implant (or tissue engineering scaffold) so that targeting is not an issue and the bioactive agents to be delivered are set free directly at the location of the implant (implant-associated drug delivery) [3]. Due to the inherent mechanical weakness of nanoporous biomaterials, these are typically applied as coating or polymer composites. According to the task of the implant, different nanoporous biomaterials can be used: nanoporous silica, nanoporous titania (in applications related to bone and dental tissue) or nanoporous platinum (for stimulating electrodes addressing the nervous system). Among the bioactive agents delivered are small-molecule drugs (antibiotics, neuroprotectiva), protein growth factors, or nucleic acids (e.g. siRNA).

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Acknowledgements:

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Small-angle neutron scattering (SANS) of porous carbons combined with in-situ physisorption measurements –linking microstructure to nanoscaled porosity

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Non-graphitic carbons (NGCs) represent an important class of materials both, in research and industrial applications. Understanding the relationship between the (micro)porosity and the sp^2-polyaromatic microstructure (graphene stacks), is crucial to understand the effects of different precursors and carbonization temperatures on the porosity in industrially used carbons (activated carbons, glassy carbons, etc.). While the microstructural parameters can be obtained from wide-angle X-ray scattering (WAXS) analysis, information on the micro/mesoporosity can be obtained from SANS and physisorption, especially with respect to the differentiation of closed and accessible porosity. Here we report SANS analysis combined with in-situ physisorption using deuterated p-xylylene of coal-tar pitch samples using the DEGAS setup established at HZB (Berlin). Major goals of this study were to link porosity to microstructure as well as investigating the impact of the carbonization temperature on opening/closing of pores.

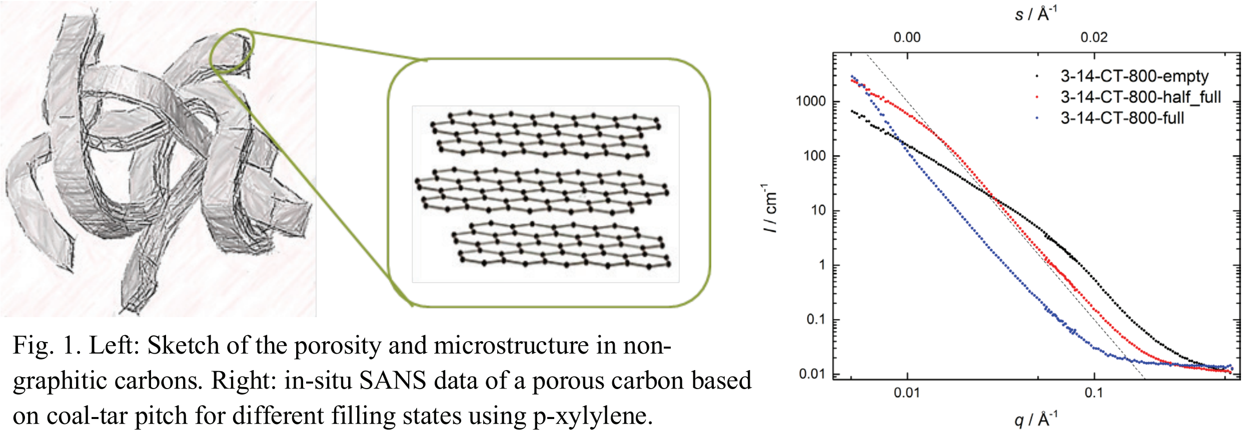

Fig. 1. Left: Sketch of the porosity and microstructure in non-graphitic carbons. Right: in-situ SANS data of a porous carbon based on coal-tar pitch for different filling states using p-xylylene.

The SANS analysis shows upon p-xylylene sorption small micropores are filled first and sharp edges are smeared out. The analyses allow for quantifying the fraction of the voids being inaccessible for p-xylylene, which is quite relevant for interpreting physisorption data. Furthermore, complementary WANS analysis show that the more disordered the carbon graphene structure is the more angled are the micropores in their shape. We found evidence that during the sorption process the polydispersity of the remaining open micro/mesopores decreases in such carbons, which is a function of the carbonization temperature. Hence, our study provides a methodology to obtain a deeper understanding in the relationship between sorption properties, nanoscaled porosity and carbon sp2 graphene structure in carbons being relevant for various applications.

Smart cotton textiles for detection/detoxification of nerve agents: role of MOF/g-C_3N_4 features

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A composite of the copper-based metal–organic framework (Cu-BTC) with oxidized graphitic carbon nitride nanospheres was synthesized and deposited on cotton textile. The surface features of the composite, g-C_3N_4 and Cu-BTC were analyzed using FT-IR spectroscopy, X-ray diffraction, sorption of nitrogen, thermal analysis, scanning electron microscopy, photoluminescence and DRUV-Vis-NIR spectroscopy. The results indicated that nanospheres of oxidized g-C_3N_4 act as linkers between the copper sites and thus play a crucial role in the composite building process. They are responsible for the development of new mesoporosity. Remarkable alterations in the optical properties and thus in photoactivity, as a result of the coordination of oxygen containing functional groups of the oxidized graphitic carbon nitride to the copper atoms of the framework, were found.

Upon the deposition of MOFgCNox on cotton textiles a stable fabric with supreme photocatalytic detoxification ability towards the nerve gas surrogate, dimethyl chlorophosphate, was obtained. Detoxification process was accompanied by a visible and gradual color change, which can be used for a selective detection of chemical warfare agents and for monitoring their penetration inside a protective layer. These smart textiles adsorbed 7 g of CWA surrogate/its detoxification products per gram of Cu. The superior performance was linked to the high dispersion of the MOF crystals on fibers, and a specific texture(mico/mesoporosity) which enhances the access of the toxic species to the active copper centers, where the decomposition takes place.

Selectively Tuned Pore Condensation and Hysteresis Behavior in Mesoporous SBA-15 Silica: Correlating Material Synthesis to Advanced Gas Adsorption Analysis

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In order to investigate the the influence of the synthesis parameters on the structural properties of SBA-15 silica, with pore diameters ranging from ca. 5 nm up to 11 nm, we have performed a systematic study of N_2 and Ar adsorption at 77 and 87 K, respectively, coupled with the application of state-of-the-art NLDFT data reduction methods. Herein, it is demonstrated that pore condensation and hysteresis behavior of inert gases in subcritical conditions confined in high quality SBA-15 samples can precisely be modulated as a function of the synthesis parameters. Synthesis conditions were found for generating SBA-15 samples that can be described entirely as a pseudo one-dimensional (1-D) pore system, i.e., in agreement with the independent open pore model.[1] However, the data also revealed that distinct synthesis conditions allow for the preparation of SBA-15 with pore evaporation properties being affected by pore blocking/corrugation effects. In the same way cooperative pore network effects were also observed during adsorption for specific SBA-15 samples, mimicking the behavior observed for materials with a pristine three-dimensional (3-D) interconnected pore network topology, such as KIT-6 silica.[2-4] Therefore, this comprehensive study shows that SBA-15 should be best regarded as a family of solids with easily adjustable porosity, ranging from corrugated and/or distorted pore systems to highly interconnected networks of channels, rather than a unique standard mesoporous silica. The effect of each different synthesis parameter on the final pore size of SBA-15 was carefully monitored, and a threshold acid concentration range for optimal mesophase tailoring was found. Such results open vast possibilities as they allow the precise design of a siliceous mesoporous material with optimized porous properties. These advances are not only significant for improving SBA-15 synthesis and accurate porosity assessment, as our methodology can be extended to related materials specifically designed for applications in which confinement effects, diffusion, and mass transport parameters are critical. Finally, our results provide a deeper understanding of textural features and shed some light on the critical need to develop data reduction methods based on models which better describe the complex reality of pore networks, including potential effect of surface roughness/heterogeneities/texture on confined fluids.

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Bimodal Mesoporous CMK-5 Carbon: Selective Pore Modification and Pore Filling

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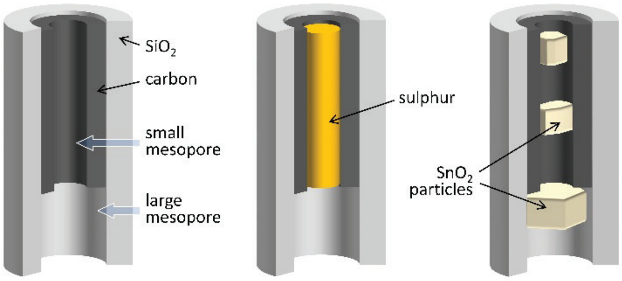
CMK-5 carbon exhibits two distinct mesopore systems. It consists of periodically arranged, linear cylindrical tubes of amorphous carbon. The voids between adjacent tubes form a continuous system of mesopores (inter-tubular pores), whereas the interior of the hollow tubes constitute another mode of mesopores (intra-tubular pores). The two pore systems can be addressed independently during the synthesis of CMK-5 (by structure replication using mesoporous SBA-15 silica as a structural mould). It is possible to load only one of the two pore systems with guest species or to modify/functionalize the pore walls of only one type of pores.



We present the synthesis of bimodal mesoporous CMK-5 carbon with selective functionalization of the intra-tubular pores: (i) Oxygen-containing functionalities at the pore walls were created by oxidative treatment with acidic persulfate solution [1]. This leads to increased polarity, as investigated by water vapor physisorption analysis. The other (inter-tubular) pore system remains unpolar, resulting in a bifunctional material with potential impact on application in catalysis or sorption. (ii) The intra-tubular pores were also individually filled with elemental sulfur, yielding a mesoporous sulfur/carbon composite material with promising properties for application as a cathode in lithium-sulfur cells [2]. Since the inter-tubular pores are still empty, a dual function emerges; one pore system hosts the guest species (sulphur), while the other pore system may be used for efficient electrolyte penetration. (iii) Likewise, we have created SnO_2 nanoparticles in the intra-tubular pores for potential application as an anode material in Li-based cells.

The materials are characterized by a variety of techniques, including N_2 and H_2O physisorption analysis, Hg intrusion porosimetry, electron microscopy, and low-angle X-ray diffraction, including an in-depth study by theoretical simulation of low-angle X-ray data [3].

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Syntheses in Ball Mills – Solvent free pathways towards porous carbons and polymer frameworks

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In the past, tremendous effort has been put into the development of novel nanostructured carbon and polymer framework materials targeting many adsorption-related applications. As a result, a wide range of high performance "designer materials" have been synthesized, most of which rely on processes that are neither scalable nor time efficient, let alone affordable or sustainable.

However, one of the main challenges in our field lies within the reduction of waste generated during the syntheses of all these materials. Therefore, solvent-free alternatives to the established conventional reaction pathways are more desirable than ever. In the recent past, mechanochemical procedures have been proven to be more than capable to tackle this problem. In a wide scope of fields, ranging from material synthesis over organic chemistry to pharmaceuticals, reactions have been carried out in ball mills. In general, these reactions proceed with high yields, short reaction times and in the absence of solvents.

By adapting classical syntheses of porous materials to the solvent-free environment of the ball mill, we have been able to tackle all of the above-mentioned problems at once. Lately, we have been able to explore the possibilities of different polymerization reactions under mechanochemical conditions.[1,2] With this, we could synthesize porous carbons with surface areas exceeding 3000m²/g, nitrogen-doped carbons, carbons with well-defined and ordered pore architecture, porous carbons-with ultra-hydrophilic surfaces, as well as covalent-organic frameworks by mechanochemical reactions in planetary ball mills.[3,4]

This new synthesis concept does not only provide an economically and ecologically favorable alternative to conventional syntheses of porous materials, it also displays a counter-intuitive momentum, since ball-milling, commonly utilized to destroy matter, can obviously be applied to construct fragile and defined framework materials.

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CPM8 | INVITED LECTURES
TUESDAY, MAY 8, 2018

Forced Intrusion of Water and Aqueous Solutions in Nanoporous Materials

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The high pressure forced intrusion studies of water in hydrophobic microporous materials such as zeolites and MOFs, is a field of research that has emerged some 15 years ago and is now very active. Many of these studies are aimed at investigating the possibility of using these systems as energy storage devices. A series of all-silica zeolites (zeosil) frameworks were found suitable for reversible energy storage because of their stability with respect to hydrolysis after several water intrusion-extrusion cycles. Several microporous hydrophobic zeolite imidazolate frameworks (ZIFs) also happen to be quite stable and resistant towards hydrolysis and thus seem very promising for energy storage applications. Replacing pure water by electrolyte aqueous solutions enables to increase the stored energy by a factor close to 3, on account of the high pressure shift of the intrusion transition. In addition to the fact that aqueous solutions and microporous silica materials are environmental friendly, these systems are thus becoming increasingly interesting for the design of new energy storage devices. We address here the theoretical approaches and molecular simulations of confined water performed in order to better understand the experimental behaviour of nano-confined water. Molecular simulation studies showed that water condensation takes place through a genuine first-order phase transition, provided that the interconnected pores structure is 3-dimensional and sufficiently open. In an extreme confinement situations such as in ferrierite zeosil, condensation seem to take place through a continuous supercritical crossing from a diluted to a dense fluid, on account of the fact that the first-order transition line is shifted to higher pressure, and the confined water critical point is correlatively shifted to lower temperature. These molecular simulation studies suggest that the most important features of the intrusion/extrusion process can be understood in terms of equilibrium thermodynamics considerations.

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Clusters, Molecular Layers and Condensate in Adsorption: Interplay between various Interactions and the Nature of the Adsorbed Phase-Gas Interface

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The mechanism of adsorption on non-polar fluids and associating fluids is dictated by the interplay between the interactions between the adsorbate molecules and the interactions between the adsorbates and the various adsorption spaces within the adsorbent solid with different surface energies and different capacities. It is commonly believed that a clustering mechanism is inherent in associating fluids, but we will show in this presentation that any adsorbates can exhibit clustering, molecular layering and condensation in adsorption systems. This results from the interplay between the various interactions mentioned above, the temperature and the loss of the adsorption space as the adsorption proceeds. We also present the physics of the thin-to-thick film transition that is a consequence of the intermolecular interactions and the nature of the interface between the adsorbed phase and the gas phase. Two adsorbates, argon and water, representative of non-polar and associating molecules, are used in Monte Carlo and kinetic Monte Carlo simulations to show the microscopic origin underlying the phenomena of clustering, molecular layering and condensate filling in adsorption on nano-structured surfaces and in confined spaces.

A novel acetic acid-fragment co-assembly method for creating defects in a copper-based metal-organic framework and its effects on methane uptakes

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Natural gas, composed of primarily methane, is regarded as a promising energy source due to its efficient and environmentally clean combustion. Adsorbed natural gas (ANG) based on highly porous materials such as metal-organic frameworks (MOFs) has been considered as one of the promising alternatives to the conventional compressed natural gas (CNG) or liquefied natural gas (LNG), which not only are costly but also have caused some safety concerns. Herein, we propose a novel acetic acid (AcOH)-fragmented linker co-assembly strategy to create defects in a copper-based MOF, HKUST-1, which is one of the best performers for methane storage. We verified the successful co-assembly of AcOH fragments into the HKUST-1 structure through various characterization methods, including ^{1}H NMR, FT-IR and XPS. The prepared defective HKUST-1 structures showed greatly increased surface areas and pore volumes compared to pristine HKUST-1 and exhibited considerably enhanced total methane uptakes at 65 bar as well as highly improved deliverable capacity between 65 bar and 5 bar. We also propose possible scenarios of defect formation in the AcOH-fragmented HKUST-1 materials from simulations of several hypothetical structures.

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Modeling of liquid Metal-Organic Frameworks

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Metal-organic frameworks (MOFs)[1], materials where inorganic units, metals or clusters, are linked together by organic ligands, have been mostly studied in their crystalline form. Their usually large specific surfaces make them promising materials for gas separation, gas storage or catalysis applications. However, amorphous MOFs were recently spotted as very highly interesting materials for applications such as reversible gas storage or harmful substances encapsulation[2]. Some Zeolitic Imidazolate Frameworks (ZIFs), a subgroup of particularly stables MOFs, have been shown to undergo thermal amorphization by melting and quenching without change in their chemical composition[3].
The crystal and the hybrid glass can be characterized, but the properties of the liquid phase, either in terms of structure or dynamics, are essentially unraveled. We performed first principles molecular dynamics simulations of three different ZIFs frameworks to get a better insight on the melting process.

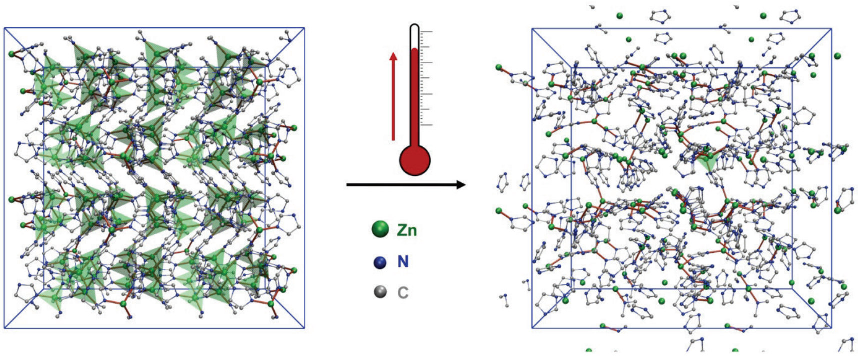

Figure 1 : From crystal to liquid, the crystalline configuration (left) and a snapshot of the liquid at 1500 K (right).

The pair distribution functions that we can compare to experimental ones were insufficient to give us a complete understanding of the undergoing mechanism for melting. In order to probe the already proposed mechanism of bond reconstruction during amorphization[3], we performed statistical analyses of the coordination network at different temperatures, in particular in the liquid state. We also adapted a mechanism used for water reorientation[4] to model the dynamics of the coordination network in the liquid. As a consequence, our work unravels the processes at stake at the microscopic level during thermal-induced amorphization in ZIFs[5].

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Transport as a tool to characterize multiscale porous media

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Hierarchical porous materials, which combine several porosity scales, are widely used in industry (separation, catalysis) to overcome slow diffusion in microporous solids (< 2 nm) and enhance access to their large surface area. Available modeling approaches for adsorption/transport in such multiscale media are limited to empirical parameters which cannot be derived from molecular coefficients. In particular, existing approaches (1) describe empirically the adsorption/transport interplay and (2) do not account for the breakdown of hydrodynamics at the nm scale. Here, I will present a multiscale model of adsorption/transport in hierarchical materials. I will first show how adsorption, permeance, and transport in such media can be described without having to rely on macroscopic concepts such as hydrodynamics [1,2]. Using parameters and coefficients available to simple experiments, we will see how transport coefficients can be obtained from statistical mechanics simple models. Then, I will present a multiscale model of adsorption and transport in hierarchical materials, which consists of upscaling molecular simulations in a lattice model [3]. Thanks to the use of atom-scale simulations, which capture the different adsorption and transport regimes upon varying the temperature, pore size, pressure, etc. this bottom-up model does not require assuming a given adsorption or flow type. I will also discuss NMR experimental results on transport in hierarchical zeolites [4].

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In-situ synchrotron X-ray diffraction upon gas adsorption and release for exploring unusual adsorption features in porous materials

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Useful information can be obtained combining powerful experimental gas and computation tools, including high resolution gas adsorption and in-situ synchrotron XRD measurements during the gas loading and release from the nanoporous voids. Our studies on equilibrium gas adsorption on different families of nanoporous materials (such as MOFs, ZIFs and zeolites) have revealed unusual structural modifications (so called gate-opening and/or breathing effects) depending on the size and polarizability of the gas probe and the interactions with the solid host [1]. In this work we provide insights on the mechanisms governing structural deformations during gas adsorption of various nanoporous solids (i.e., ZIF-8, ZIF-67, MFI, FAU, LTA zeolites), combining in-situ adsorption and high resolution powder diffraction. The in-situ synchrotron high resolution powder XRD measurements combining various probes (e.g. N_2, Ar, CH_4, CO_2, O_2) and temperatures were conducted at the Spanish CRG at ESRF, in a controlled environment chamber, that allowed the fine control of the gas dosage, sample outgassing under vacuum and temperature control during the measurements [2]. In the case of ZIF-8, we have shown that the gas-induced deformation does not affect the cell structure of the pristine material, although it does modify its gas uptake. This process is governed by the polarizability, molecular size and shape of the gas adsorbed, and it is originated in the rearrangement of the moieties inside the cavities when a threshold gas pressure is attained upon adsorption. A similar effect was detected for an isomorphic material with a different cation, showing that this phenomenon is not affected by the electronic structure of the metal defining the structure of the framework. We have also explored all silica MFI zeolite, since this material has a bi-stable behavior controlled by the gas pressure as external stimulus, provoking an outstanding structural transformation [3,4]. Data has evidenced that the origin of the gas-induced structural changes, would be attributed to changes in the gas phase rather than to a solid phase transition from the monoclinic to orthorrombic phase.

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Synchrotron XRD and inelastic neutron scattering studies under operando conditions to understand structural phenomena in ZIFs

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Zeolitic imidazole framework materials (ZIFs) are a very exciting class of MOFs with very interesting structural properties upon an external stimulus (for instance upon gas adsorption, after a thermal treatment or under high-pressure conditions). Despite their rigid zeolitic topology, sodalite (SOD) materials like ZIF-8, ZIF-7, ZIF-65 and ZIF-90 have shown to exhibit associated structural changes upon N_2 or CO_2 adsorption, for instance gate-opening phenomena, phase transitions, swinging of linkers, etc. Traditionally these changes have been evaluated using gas adsorption at cryogenic temperatures (for instance N_2 adsorption at 77K or Ar adsorption at 87K) or CO_2 adsorption at 298K [1-3]. Experimental results clearly show the presence of well-defined steps or jumps at specific relative pressure regions. Although adsorption isotherms anticipate the presence of these structural changes through specific alterations of the isotherm profile, it is *a priori* rather difficult to understand the reason behind these observations.

In this study we will show how the combination of synchrotron X-ray powder diffraction and inelastic neutron scattering under operando conditions can provide valuable knowledge to complement the adsorption measurements. The combination of these two techniques upon nitrogen or carbon dioxide adsorption is of paramount importance to understand the nature of these changes, their reversibility, temperature and pressure dependence, etc.

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Acknowledgements:

Multi-scale pore network characterization of building materials using micro-CT and FIB-SEM tomography

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Three-dimensional (3D) analyses of the pore structure of building materials are becoming progressively more important in recent years for more accurate interpretations and simulations of their properties and performances. These building materials are characterized by a large variety in pore radii (e.g., nanometer to millimeter scale). The problem of constructing a pore level model at the representative scale, must be solved by including information from each length scale of this multi-scale system.

Two different imaging techniques are used to visualize the pore structure at different scales. On a micrometer scale computed tomography (CT) has proven to be an excellent and versatile tool to perform these analyses non-destructively. To visualize even smaller pore structures of building materials on the nanoscale, scanning electron microscopy combined with focused ion beam (FIB-SEM) is used. Post processing of the 2 dimensional FIB-SEM images results in a reconstruction of the 3D pore space. Both techniques allow calculating relevant parameters such as pore size, shape and orientation in 3D. Additionally, the pore network is also indirectly characterized by mercury intrusion porosimetry (MIP), resulting in a validation of the results of the direct imaging techniques with a multi scale MIP analysis.

Moreover, building materials are often non-granular in nature, resulting in pore networks comprising of complex pore shapes. Hence, these materials are ideal test cases for pore-shape analysis and the study of the Representative Elementary Volume (REV) of different parameters. Because the used datasets transient different length scales, the results of the REV analysis will be compared to the observations of Norris et al. (1991) and Nordahl and Ringrose (2008) for geological samples. They both suggested the existence of different REV sizes at different scales which has major implications when determining a relevant upscaling strategy.

In order to come up with a trans-scale model, the CT and FIB-SEM datasets need to be superimposed to create a combined network which holds information of both length scales. In the future this model can then be used to simulate the moisture storage and transport properties of building materials.

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Probing potential of the confinement – study of in-cage dynamics of molecular hydrogen in clathrates hydrates.

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Understanding how to control the mobility and dynamic activity of molecules and ions by confinement is highly significant both from academic point of view and for the broad range of applications based on the confinement of ions and molecules. In porous materials the molecular confinement is often realized by means of weak Van der Waals interactions between the stored molecule and the pore surface. Thus the core question is how to modulate such interactions and how to make the molecules less or more mobile in order to obtain the desired properties. Here the role of confinement size is of fundamental importance.

We have studied in-cage dynamics of confined molecular hydrogen as a function of confinement size using nanoporous clathrate hydrates with hydrophobic nanocages of two different dimensions. Clathrates hydrates are nanostructured porous materials, where hydrogen is stored in cages of two different sizes of 0.75 and 0.946 nm, resulting in storage capacity of up to 5.3 wt.% [1]. Besides high technological interest clathrate hydrates are particularly suitable model systems to study the role of confinement since the interactions between the framework of the clathrates and H_2 are of the same hydrophobic nature in both cages. We have found that by varying the size of the pore by only 20 % in the effective radius we can modify the diffusive mobility of confined hydrogen in both directions, i.e. both reducing and enhancing mobility compared to the bulk. In the smaller cages of clathrate hydrates with a mean size of 0.795 nm hydrogen is localized in the center of the cages even at temperatures up to 200K [2]. Moderate increase of the confinement to 0.946 nm leads to the onset of jump diffusion between tetrahedrally shaped sorption sites in large cages with separation length of 2.79±0.23 Å [3] already at T=10 K, where bulk hydrogen is frozen at ambient pressure. The observed difference in mobility between small and large cages can be understood as a dimensional phenomenon caused by the modulation of cage potentials as a function of the cage size. The localization of hydrogen in small cages indicates the existence of molecular traps of potential minima in the center of the cage, matching the molecule size and leading to reduced sorption pressure and enhanced gas release temperature in binary clathrates. The increase of the cage dimension leads to a flatter potential that, in contrast, promotes intra-cage mobility. Similar mechanism could play a role in the processes of electrochemical storage or of the confinement of water.

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Fluid Flow and Permeation within a Hierarchical Porous Medium with Transverse Permeability Discontinuity

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Understanding mass transport within hierarchical porous systems is important in many fields, including supercapacitors, PEM fuel cells, tissue engineering scaffolds, drug delivery, and heterogeneous catalysis. A key issue in transport in such systems is the extent of mass and momentum exchange between different levels in the hierarchy. In this work, magnetic resonance imaging (MRI) velocimetry methods have been used to study fully developed axially symmetric fluid flow within a model porous medium with cylindrical symmetry and a transverse permeability discontinuity (see Figure 1). Spatial mapping of fluid flow resulted in radial velocity profiles. The high spatial resolution achieved for these profiles allowed the estimation of the slip in velocities at the boundary between a clear central channel and macroporous walls. The profiles were compared to theoretical velocity fields for a fully developed axially symmetric flow in a cylinder with porous walls as derived from the Joseph and Beavers, and the Brinkman, boundary models. Velocity fields were also computed using pore-scale Lattice Boltzmann Modelling (LBM), where the assumption about the boundary could be omitted. Both approaches gave a good agreement between theory and experiment, although the LBM velocity fields followed experiment more closely. This work shows the great promise for MRI velocimetry methods in addressing the boundary behavior of fluids in opaque heterogeneous porous media.

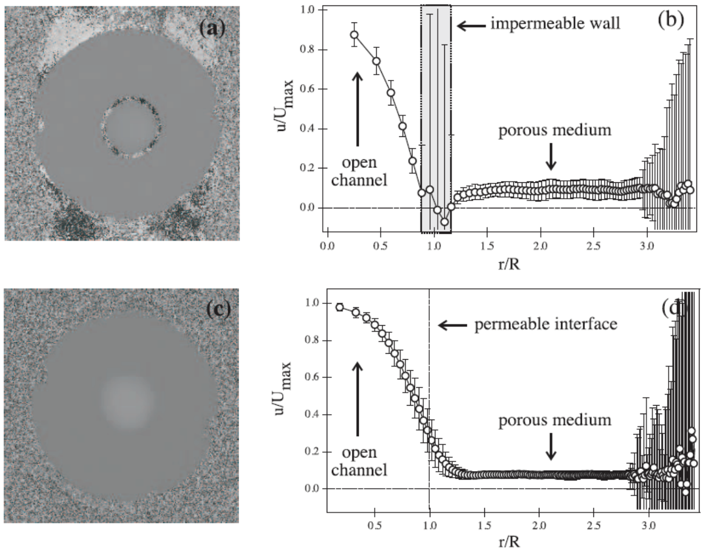

Figure 1. Velocity maps (a,c) and corresponding azimuthally averaged radial velocity profiles (b,d) in the absence (top panels), and in the presence (bottom panels), of the fluid momentum transport across the channel-wall interface.

Coupling of volumetric and calorimetric devices for simultaneous measurements of adsorption isotherms and enthalpies

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Since temperature strongly influences breakthrough curves, modeling and design of adsorption processes requires a precise knowledge of adsorption enthalpies. The adsorption enthalpy is a function of the adsorbent's loading, so a simultaneous measurement of both quantities is desirable. Therefore a measurement technique for the coupling of calorimetric and volumetric equilibrium measurements in one device was developed.

A commercially available volumetric adsorption measurement device is extended by a calorimetric unit which measures the differential pressure between two identical gas volumes located in a water bath at a defined temperature. One of these gas volumes surrounds the sample cell where adsorption occurs, whereas the second surrounds a reference cell filled with inert glass beads. Due to the exothermic adsorption process the temperature in the sample cell rises. The resulting heat flux through the surrounding gas volume into the water bath causes a temporary increase in temperature and pressure of the gas which can be measured as a pressure difference to the reference volume. The adsorption enthalpy can be calculated from the pressure difference curve using calibration measurements.

Figure 1 exemplarily presents adsorption isotherms (left) and enthalpies of adsorption (right) of n-alkanes on a 13X zeolite at 25°C. The data underlines the load dependence of the adsorption enthalpy and allows conclusions to interactions and mechanisms during adsorption.

In the talk the basic principle and the technical implementation into a device as well as some selected experimental results will be discussed.

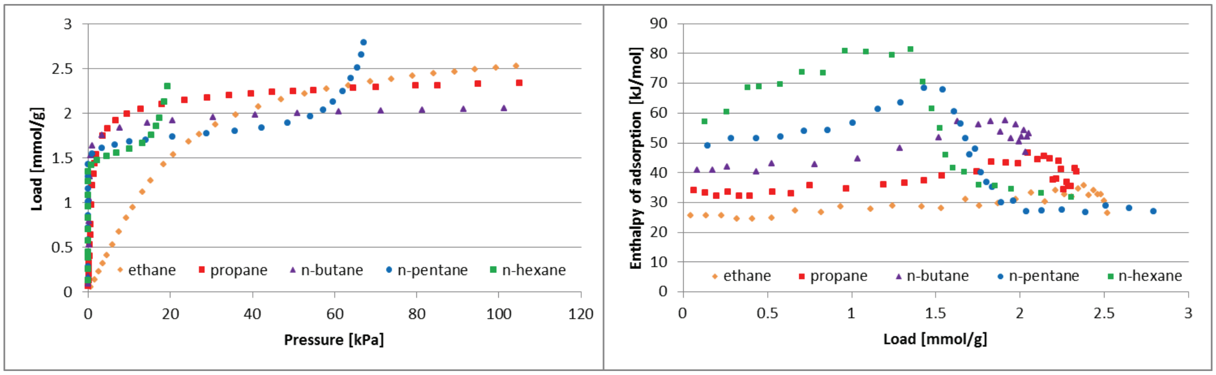

Fig. 1. Adsorption isotherm (left) and enthalpy of adsorption (right) of n-alkanes on a 13X zeolite at 25°C

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Two-fluid model for supercritically adsorbed films of hydrogen and methane in nanoporous materials

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The search for clean, sustainable automotive fuels has driven numerous studies of sorption-based hydrogen storage for hydrogen fuel cell vehicles and methane storage for low-carbon-footprint, near-zero-emission internal combustion engines. Storage by adsorption is fully reversible, achieves fast fill/discharge demands by simple pressurization/depressurization, and operates at much lower pressure than compressed hydrogen or methane. We have investigated the density, thickness, and volume of adsorbed hydrogen films at 77 K and methane films at 298 K in a variety of porous carbons synthesized at the University of Missouri [1, 2]. Samples include monoliths, powders, activated carbons, and pyrolytic carbons. The films, adsorbed at supercritical conditions, are monomolecular. The analysis decomposes stored hydrogen and methane into a high-density adsorbed film and low-density non-adsorbed gas (two-fluid model), coexisting in the pore space, and determines the fraction of pore volume occupied by the two phases. Saturated film densities, film thicknesses, and film volumes are determined from high-pressure excess adsorption isotherms.

Saturated hydrogen film densities at 77 K are 100-120 g/L across all samples at pressures as low as 35-70 bar. This is 1.4-1.7 times the density of liquid hydrogen at its normal boiling point, 71 g/L (20 K). Experimental film thicknesses are 0.30-0.32 nm, and fractions of total pore volume filled with high-density film are 0.25-0.53. Thus high storage capacities, in excess of liquid hydrogen, can be achieved at 77 K in appropriately engineered nanoporous carbons.

Saturated methane film densities at 298 K are 390-420 g/L, comparable to that of liquid methane at its normal boiling point, 420 g/L (112 K). Experimental film thicknesses are 0.40-0.41 nm. Thus the adsorbed films of methane may be paraphrased as “liquid methane at room temperature.”

The dense films occur at a temperature $T/T_c = 2.3$ and 1.6, for hydrogen and methane, where $T_c =$ 33 K and 190 K is the respective liquid-gas critical temperature, above which no bulk liquid exists at any pressure. The high-density films above T_c do not contradict the non-existence of bulk liquid: the film is not a bulk, 3D phase, but a monomolecular 2D phase. Monte Carlo simulations confirm the observed high density and small film thickness. They exhibit that film density and film volume remain constant up to pressures at which the gas density is ~80% of the saturated film density, and that the film thickness, ~0.30 nm, equals the H_2-H_2 closest approach distance. The picture that emerges is that the adsorption potential pins hydrogen molecules to the surface as densely packed as possible without lateral repulsion between the molecules.

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X-ray CT imaging of gas adsorption to characterize nanoporous materials

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Imaging techniques constitute a novel paradigm in characterization methods of porous media; X-ray Computed Tomography (CT) is of particular interest because it enables the non-destructive determination of spatially resolved properties[1]. However, bench scale laboratory systems are still limited to voxel sizes above 1 μm^3, and therefore do not allow visualizing micro- and meso-porosity (≤ 50 nm) that is ubiquitous in both natural (e.g., clay, coal, shale) and most porous materials used in the chemical industry (e.g. adsorbent materials). The most widespread technique for the characterization of nanoporous solids indeed is gas adsorption. While the interpretation of sub-critical adsorption isotherms in terms of pore size, pore structure and connectivity is being continuously refined[2], gas adsorption remains a technique that only provides bulk (macroscopic) information.

The images obtained from X-ray CT scans contain spatially resolved quantitative information related to the local density. Based on this observation, Pini[3] recently showed that it is possible to extract the excess adsorption from the subtraction of scans of a porous solid taken in the presence of an adsorptive gas and of an inert gas (e.g. Helium). This work has been extended here by developing the relevant experimental and analysis protocols to measure full excess adsorption isotherms by X-ray CT imaging over the pressure range 1– 30 bar. By applying the devised protocols to fixed beds of commercial zeolite 13X pellets and activated carbon rods, we measured spatially distributed adsorption isotherms with a medical CT scanner, as illustrated in Fig. 1. This work provides a novel way to probe nanoporosity of heterogeneous porous media in multiple dimensions, across multiple scales and in a non-destructive way. As such, it is expected to bear significant importance in the characterization of nanoporosity within natural and synthetic porous media, where 3D information on the pore space is essential for the accurate description of gas transport.

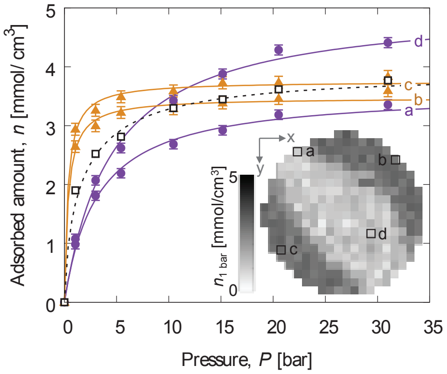

Fig. 1 – X-ray CT image taken at 30 bar CO_2 of a composite bed containing Zeolite 13X and an activated carbon pellets. Voxel resolution ~10 mm^3 (2.3×2.3×2) mm (bottom right). Adsorption isotherms of selected voxels in the central slice of the bed (solid symbols), and the corresponding Langmuir fits (lines). Comparison to the bed-averaged adsorption isotherm (empty squares).

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What effect does confinement have on the structure of liquid benzene?

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Confined liquids are subject of research in many areas such as geology, biology, food and drug preservation, and heterogeneous catalysis. Due to reduced dimensionality and large surface interface effects, liquids that are subjected to some geometric constraints, usually on nanoscale, can have different properties than in standard bulk conditions. Understanding the structure of confined liquids can explain why these properties change.

Molecular-scale structure of a complex disordered system comprising liquid reagent, *i.e.* benzene-d_6, confined in porous catalyst has been studied by total neutron scattering. MCM-41 was used as the catalyst support which simplifies the analysis of neutron scattering data, because it is an amorphous material with highly-ordered hexagonally arranged cylindrical pores. The model of MCM-41, as well as a three 3D model for liquid under confinement were constrained by the experimental data by utilization of Empirical Potential Structure Refinement (EPSR),[1] and were used for study on local ordering in the system. The structural information expressed by radial, site-site and spatial density functions for confined benzene were compared with the corresponding bulk phases.[2] Additionally, cylindrical distribution functions showing the arrangement of atoms and molecules across a pore and orientational cylindrical distribution functions showing the preferred orientations of molecules with respect to the pore walls were calculated. These properties were also calculated for confined cyclohexane-d_{12} and cyclohexene-d_{10}.

Analysis of the cylindrical distribution functions showed that all chosen confined liquids form layers across a pore. Molecules form seven coordination layers counted across the pore diameter, from which the closest ones were better pronounced. Analysis of radial distribution functions indicates the disruption of local ordering when compared to the bulk liquid, which is pronounced by change in the function shape. This is particularly observed for benzene-d_6. This is confirmed by an analysis of the spatial density functions, which, for benzene, shows different preferable positions for surrounding parallel molecules. Orientational cylindrical distribution functions in general show a tendency for molecules to orient with the plane of the ring flat against the pore wall.

For the first time, to our knowledge, three liquid reagents, different than water, in confinement have been fully examined by total neutron scattering. The obtained structural properties show that the structure of liquid in confinement is significantly different than in corresponding bulk phase. Developing the procedure for analyzing confined liquids in catalyst support pores enables subsequent modelling of reacting systems structure in snapshots.

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Size-Controllable MOF Composite Particles for Adsorptive Separations: Formulation, Characterization and Study of Mass Transfer Resistances

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Recovery of useful chemicals produced in fermentation processes is complicated by the low concentration of those products in the fermentation broth. The excess of water results in large energy costs if distillation is used. Adsorption has been identified as an efficient alternative for the traditional energy-intensive distillation technique. Among various porous materials, including zeolites, active carbons and metal-organic frameworks (MOFs), we found that that hydrophobic MOFs such as ZIF-8 show interesting properties, giving perspectives for an economical and low energy-intensive production of biofuels and beochemicals such as biobutanol [1].

The formulation of the ZIF-8 MOF material into a resistant structure is a key aspect towards its implementation into an actual separation process. Therefore, resistant MOF composite beads were produced by combining polymers with ZIF-8 crystals under different conditions. The formulation method, which easily allows varying the particle size, will be presented. In addition, the adsorptive properties, studied under dynamic and static conditions in liquid and vapor phase, as well as the stability of the composite particles under chemical and mechanical stress will be discussed. Mass transfer resistances related to the formulation will be highlighted. Additional results obtained by various characterization techniques, such as argon and mercury porosimetry will also be presented. The results of these different experiments demonstrated that the formulation method allows to produce resistant ZIF-8 MOF composite particles with controllable size and with limited change in properties of the original material, which are important for the efficient adsorptive recovery of bio-butanol. The formulation method is, moreover, expected to be applicable to any other nanoporous material.

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An experimental method for screening the effect of water vapour on gas adsorption performance: Application to CO2 capture from flue gas in MOFs

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The influence of water on the adsorption of gases is a crucial point in the development of new sorbent, as water is an ever-present component in many industrial streams. Adsorption studies under humid conditions have been reported on promising materials for CO_2 capture from flue gas and have often shown the detrimental effect of H_2O on adsorption performances, as observed, for example, for zeolites.[1, 2] Indeed, small amounts of water can significantly affect the CO_2 -adsorption properties owing to its strong adsorption at hydrophilic sites, which thus prevents CO_2 from interacting with these strong adsorption sites in the material. The diversity of CO_2 -adsorption mechanisms in the presence of water highlights the necessity to develop experimental methods to rapidly pre-select the adsorbents of interest. Much work presented to date involves column breakthrough experiment or the recording of CO_2 adsorption isotherms after exposure to controlled amount of water. More recently, a high-throughput instrument for the measurement of adsorption equilibrium was developed giving further insights about the amount of water adsorbed, which is directly linked to regeneration energies.[3] All these techniques result in good accuracy when studying the effect of water on CO_2 -adsorption performances but they are time consuming, require specific instrumentation and imply complicated data processing.

In this work, a simple laboratory scale protocol is proposed which enables the evaluation of the effect of adsorbed water on CO_2 uptake. Herein, a simple thermogravimetric analysis (TGA) apparatus was adapted to render a simplified screening method to rapidly evaluate the effect of water on gas adsorption performances using a minimal amount of sample. Indeed, stepwise outgassing of a pre-humidified sample and CO_2 adsorption/desorption between each step gives the possibility to follow the effect of water pre-adsorbed on CO_2 uptake. This method was then applied to study the effect of water on CO_2 adsorption performances for 45 MOFs and were compared to reference zeolites and activated carbons. With this method, it is possible to class materials with different trends in CO_2 uptake with varying amounts of preadsorbed water. Comparing loss in CO_2 uptake between “wet” and “dry” samples with the Henry constant calculated from the water adsorption isotherm results in a semi-logarithmic trend for the majority of samples allowing predictions to be made. Outliers from this trend may be of particular interest and an explanation for the behavior for each of the outliers is proposed. This thus leads to propositions for designing or choosing MOFs for CO_2 capture in applications where humidity is present. Then, the regeneration and the stability of the three most promising adsorbents selected from the screening step for CO_2 capture were investigated by cycling experiments. Finally, a correlation between an estimation of the interaction of water with the material and CO_2 -capacity loss in the presence of water has been established.

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Immersion calorimetry study of textural and chemical modifications of MOFs

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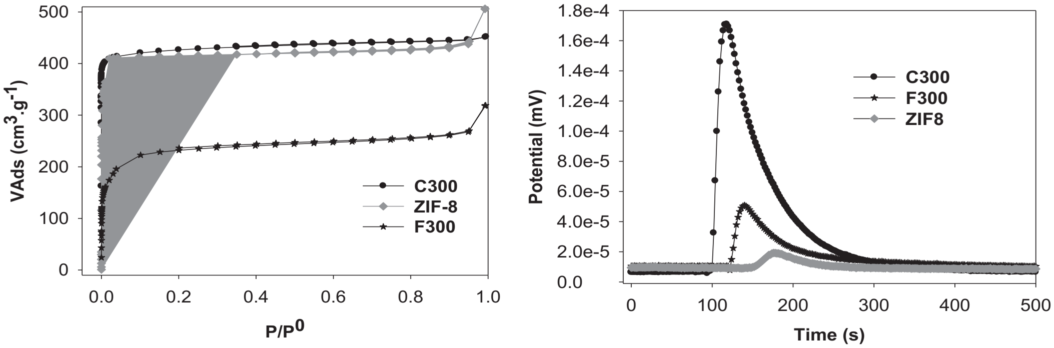
Metal-organic frameworks (MOFs) are interesting solids that have captured the attention in the porous solids research field, because this kind of structure includes a metal center with organic linkers as secondary building units (SBUs). There are many advantages related to MOF materials: (i) high textural parameters and tunable pore size according to the organic linkers; (ii) it is possible by postsynthetic treatments to modify the surface according to target molecule, also the accessibility and reactivity [1].

The immersion enthalpy of a porous solid in a liquid can be used to evaluate the porous structure and parameters associated with the surface chemistry of the solid. The immersion enthalpies of the various MOFs: C-300, F-300 , ZIF-8 and their modifications, in benzene, dichloromethane, water and ethanol were determined using a heat conduction calorimeter. They are probe molecules of specific and dispersive interactions, thus C_2H_5OH has a polar (hydrophilic) and nonpolar (hydrophobic) part; water interact to hydrophilic surfaces, and simple organics molecules like benzene and dichloromethane can establish dispersive interactions [2]. The results obtained by determining the immersion enthalpies in every liquid were exothermic with values between 201 to 10 $J.g^{-1}$; the potentiograms of the immersion of the start solids in benzene are depicted in Figure 1, also the N_2 isotherm.



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Assessing adsorption induced deformation of advanced nanoporous materials with X-ray and neutron scattering

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Advanced functional materials for sensing, actuation, or energy storage are often based on highly porous materials with large surface area. They are typically organized at several length scales and their functionality critically depends on the structural details at the nanometer scale. The monitoring of structural changes due to the interaction of the internal solid surface with guest atoms, molecules, or ions calls for non-destructive, bulk-sensitive *in-situ* techniques, with small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) belonging to the most important methods in this respect.

My first example will deal with the interaction of fluid guest phases with the solid pore walls of nanoporous silica, leading to a fluid-pressure dependent, non-monotonous deformation of the material. By using tailor made materials with ordered mesopores, this deformation can be monitored via the pore lattice strain from *in-situ* SAXS or *in-situ* SANS. The structural origin for the macroscopic adsorption-induced mechanical deformation of complex systems such as macroscopic monoliths with hierarchical porosity [1], or nanoporous thin films on non-porous substrates [2] will be discussed, both systems being promising model systems for actuation devices.

The second example deals with structural studies of aqueous electrolytes in nanoporous carbons as a function of an applied voltage. The results from such model supercapacitors demonstrate that *in-situ* SAXS from disordered carbon electrodes together with new ways of data analysis allow far-reaching interpretation of ion storage mechanisms and related predictions about optimum pore geometry [3]. Moreover, electrodes based on ordered mesoporous carbons allow assessing electrosorption induced deformation of the carbon electrodes *in-situ* as a function of applied voltage [4].

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Flexible MOFs for gas separation – a case study based on static and dynamic sorption experiments.

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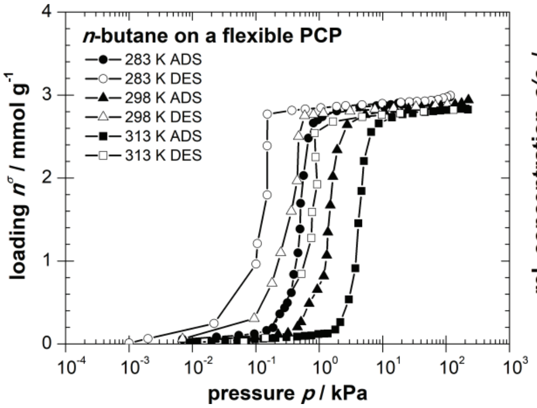
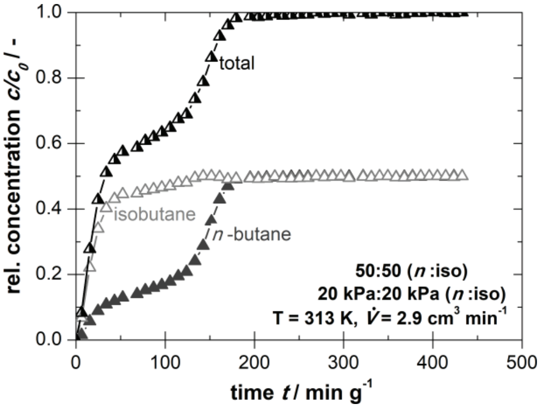
Porous metal organic frameworks (MOF's) can be categorized into rigid and structurally flexible compounds. The latter change their structure influenced by external stimuli. Whether the corresponding phenomena such as gate opening or breathing could be utilized for gas separation applications, or not, is subject to ongoing research and controversial discussions.

In this work, two structurally flexible MOFs were selected for exploring guest-induced structural changes by adsorption of C4-hydrocarbons. Pure gas sorption isotherms of n-butane, isobutane, 1-butene and isobutene reveal a stepwise increase of the surface excess loading associated with gate opening. Based on these isotherms, dynamic sorption experiments with one- and two-component adsorptives have been carried out on a packed bed at different inlet concentrations suggested by the gate opening pressure determined in the isotherm measurements. This leads to stepwise breakthrough curves being affected by the entry concentrations. We discuss the chances and limitations originating from a flexible network transition on potential separation applications.





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Structural transformations of methane adsorbed in MOF-5 model framework

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Phase changes are ubiquitous in nature, and transformations between solid structures represent a large group of them. They are usually reported on phase diagrams, as coexistence lines between different structures. The phase diagrams, well established for macroscopic 3-dimensional (3D) materials, change drastically when the material's dimensions are reduced to few nanometers, or if the material is confined in a nano-pore. At the nanoscale the positions of coexistence lines on the phase diagrams are shifted and their new locations depend mainly on the size and shape of the nano-confinement, the structure of the confining walls, and their interaction with the confined substance. Here we show that it is possible to induce structural transformations in a confined system by simply varying the number of molecules adsorbed in the pore. We found that the mechanism of these novel, adsorption-induced structural transformation in nano-pores differs from that of well-known capillary condensation. The confined, equilibrium structures are not characterized by mean positions of molecules but rather by a probability distribution of molecular positions around adsorption centres. The character of transformation depends on temperature: it is strongly discontinuous at low temperature but evolves into a continuous transition when the temperature increases.

In-situ Neutron Scattering Observation of Adsorption-Induced Expansion in the Interlayer Spacing of Graphene Oxide Frameworks

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During physisorption it is *generally* assumed that the solid remains inert. However, as the adsorbate molecules go into the pores it is possible that the adsorbant will experience structural changes [1,2]. In the past, changes have been observed in subcritical conditions, e.g. the Metal Organic Frameworks "gate opening transitions" [3]. Here we focus on structural changes under supercritical conditions in Graphene Oxide Frameworks (GOF) [4,5]. Using *in situ* neutron scattering at the University of Missouri Research Reactor (MURR), we have observed an increase of the interlayer spacing of GOFs during adsorption of three supercritical gases (hydrogen, methane, xenon) in the 0-150 bar range (Fig. 1). (The GOFs were synthesized by the insertion of diboronic acid (DBA) molecules between layers of graphene oxide. [5]) We observe an approximate *law of corresponding states* where the layer expansion can be mapped into a quasi universal curve (vs. molar excess or absolute adsorption) when adjusted by the critical temperature of the adsorbed gas. Comparison of the experimental findings with molecular dynamics simulations suggest possible structures for the GOF-DBA pores (Fig. 2).

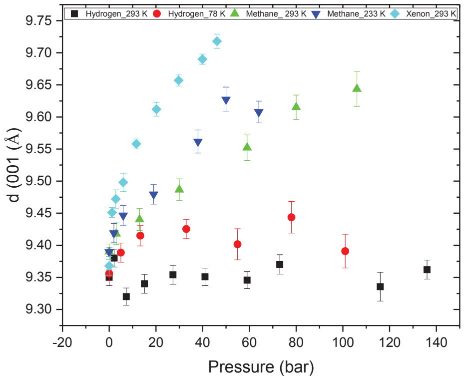

Fig. 1. Interlayer expansion vs. pressure for H_2 (293 K, 78 K), CH_4 (293 K, 233 K), and Xe (293 K).

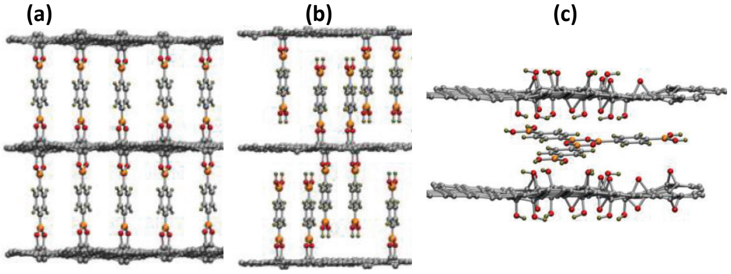

Fig. 2. Suggested models for GOF-DBA structures: a) *Cross-linked* with covalent bonds on both sides; b) *Pillared* with covalent bonds on one side and van derWaals interactions between pillars; and c) Horizontal *fluid* linker molecules stabilized by Van der Waals bonding with oxygen groups.

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Prediction of carbon dioxide breakthrough in “gating” adsorbents using osmotic framework adsorbed solution theory

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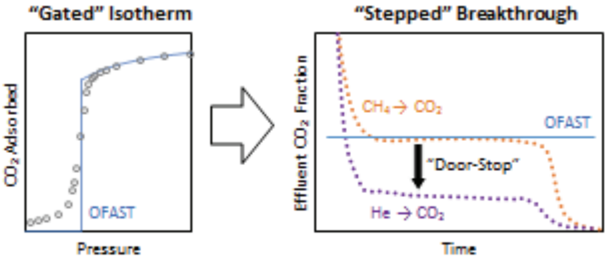
An experimental and theoretical study was conducted of the breakthrough performance of the flexible metal-organic framework $Cu(bpy)_2(BF_4)_2$ (bpy = 4,4’-bipyridine), commonly referred to as ELM-11. Pure CO_2, He, and N_2, as well as binary gas mixtures of these species, were used to perform breakthrough column experiments on ELM-11, a latent porous crystalline solid that possesses both a highly ordered network and structural transformability[1]. ELM-11 exhibits a stepped breakthrough curve for CO_2 not seen for rigid adsorbents. By comparing the step heights observed in the experimental breakthrough curves with the gating pressure predictions obtained from osmotic framework adsorbed solution theory (OFAST)[2], it is shown that the OFAST method can accurately predict the occurrence and height of the steps observed in the breakthrough curves of the flexible metal organic framework. For specific gas mixtures, the ELM-11 breakthrough curves reveal a “door-stop” type effect[3], wherein the observed step heights for CO_2 breakthrough curves are reduced when the gas mixture contains species that possess a small kinetic diameter, such as helium.



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Raman spectroscopy studies of the terahertz vibrational modes of flexible pillared layer MOF

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Low-frequency vibrations, typically appearing below 100 cm^{-1} (terahertz region), contribute considerably to the heat energy transport and, consequently, to the physical properties of the materials, but also often are the finger prints of dynamic systems (for example, DNA, proteins, amino-acids, etc.). Moreover, they are highly sensitive to conformational changes [1]. Low-frequency lattice vibrational modes have also been discussed to play a crucial role in phase transformation process of switchable metal–organic frameworks (MOFs) [2].

The pillared layer MOF $Ni_2(ndc)_2(dabco)$ (ndc – 2,6-naphthalenedicarboxylate, dabco - 1,4-diazabicyclo[2.2.2]octane), also known as DUT-8(Ni) (DUT – Dresden University of Technology) can be synthetized in “rigid” and “flexible” form, depending on the synthetic conditions [3]. The rigid version, consisting of nano sized crystallites, can be desolvated without any phase transition and shows a typical “Type Ia” nitrogen physisorption isotherm at 77K. In contrast, the flexible form, crystalizing as macro crystals, undergoes a transformation into a closed phase upon desolvation and can be reversibly transformed into the open phase by adsorption of gases or liquids.

We applied the Raman spectroscopy to study the low-frequency vibrations of rigid as well as flexible form of DUT-8(Ni) framework. Both, the open and the close pore phases could be unambiguously identified by breathing mode bands at 23 cm^{-1} and 60 cm^{-1} in the corresponding Raman spectra, showing efficiency of the technique for monitoring the flexibility in MOF materials, as well as on differences in the lattice vibrations of two phases. Born-Oppenheimer Molecular Dynamics simulations showed that observed low-frequency bands indeed correspond to the oscillation of the breathing mode along the diagonals of the pore channels. Moreover, the directional character of low-frequency vibrations in flexible version of DUT-8(Ni) could be visualized by orientation dependent Raman spectroscopy experiment.

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CPM8 | INVITED LECTURES
WEDNESDAY, MAY 9, 2018

Modeling dynamics of confined fluids: from adsorption to membrane separations

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In this presentation, we discuss a theoretical approach to modeling the relaxation dynamics for fluids in mesoporous materials called dynamic mean field theory (DMFT). DMFT is a theory of the dynamics that is also consistent with the thermodynamic picture from classical density functional theory. In addition to providing quantitative information about the adsorption/desorption dynamics, the theory also yields visualizations of condensation and evaporation processes associated with the filling and emptying of porous materials by fluids. A remarkable feature of DMFT is that the nucleation mechanisms in phase transitions of confined fluids are emergent features of the theory.

DMFT also provides a theory of the non-equilibrium steady states encountered in mesoporous membrane separations and we illustrate this with an application to volatile organic compounds separations. An important aspect of these systems is the formation of partially condensed states in which the fluid is liquid-like at the high-pressure end of the membrane while vapor-like at the low-pressure end. Such states have been assumed in previous modeling work but appear spontaneously in DMFT calculations. We also present recent work on using non-equilibrium molecular dynamics to assess the predictions of DMFT.

Measurement of Water Adsorption Equilibrium and Kinetics Using the ZLC Technique

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We present a new configuration of the zero length column apparatus designed specifically to measure water adsorption equilibrium and kinetics starting from high relative humidity conditions. We demonstrate its use using water on different adsorbents including mesoporous materials showing non-type I isotherms.

The initial study was shown to reproduce with high accuracy the desorption curves generated using a Quantachrome Aquadyne gravimetric system, including scanning desorption curves in the hysteresis region. The significant improvement gained by using the ZLC lies in the time required for generating the desorption curves as well as the fact that thousands of equilibrium points are obtained from a single experiment. The full characterisation of a sample is reduced to one week compared to 6 to 8 weeks on the gravimetric system, therefore indicating a significant potential in using this approach to measure water adsorption isotherms and characterize the properties of nanoporous materials.

Results will be presented, both below and inside the hysteresis region. Experiments at higher flowrates reveal that the kinetic behaviour in the hysteresis region is quite complex and further analysis is required.

How to Interpret Ultrasonic Measurements on Fluid-Saturated Nanoporous Solids?

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Recent progress in extraction of unconventional hydrocarbon resources, in particular shale gas, has ignited the interest in the studies of fluid-saturated nanoporous media. Since many thermodynamic and mechanical properties of nanoscale solids and fluids differ from the analogous bulk materials, it is not obvious whether wave propagation in nanoporous media can be described using the same framework as in macroporous one. Prior to approaching media as complex as shales, it is necessary to get a thorough understanding of wave propagation in simpler nanoporous media, e.g. a widely studied Vycor glass.

Here we test the validity of classical Gassmann theory of wave propagations in saturated media [1]. We consider the literature data on longitudinal and shear ultrasonic velocities in nanoporous Vycor glass as a function of pressure of n-hexane and argon vapors respectively [2,3]. The quantitative testing of the Gassmann theory on Vycor glass requires the knowledge of the bulk modulus of the solid nonporous glass K_S, which is impossible to measure directly. We propose to estimate K_S from the so-called pore-load modulus obtained from measurements of the adsorption-induced deformation [4]. Furthermore, comparison of this estimate with the estimates from the elastic effective medium theory gives a recipe for estimating K_S when adsorption-induced deformation data are not available. The fluid modulus can be calculated according to Tait-Murnaghan equation at the solvation pressure in the pore [5]. Substitution of these parameters into Gassmann equation provides predictions consistent with measured data. Our findings set up a theoretical framework for investigation of fluid-saturated nanoporous media using ultrasound.

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Diffusive Transport in Pores. Tortuosity and Molecular Interaction with the Pore Wall

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Inspired by previous experiments over a less extensive selection of pore sizes [1,2], we measured [3] the self-diffusion of neat water, dimethyl sulfoxide (DMSO), octanol, and the molecular components in a water−DMSO solution by ^{1}H and ^{2}H NMR diffusion experiments for those fluids imbibed into controlled pore glasses (CPG). Their highly interconnected structure is scaled by pore size and is supposed to exhibit invariant pore topology independent of the size. The nominal pore diameter of the explored CPGs varied from 7.5 to 72.9 nm. Hence, the about micrometer mean-square diffusional displacement during the explored diffusion times was much larger than the individual pore size, and the experiment yielded the average diffusion coefficient. Great care was taken to establish the actual pore volumes of the CPGs. Transverse relaxation experiments processed by inverse Laplace transformation were performed to verify that the liquids explored filled exactly the available pore volume. Relative to the respective diffusion coefficients obtained in bulk phases, we observe a reduction in the diffusion coefficient that is independent of pore size for the larger pores and becomes stronger toward the smaller pores. Geometric tortuosity governs the behavior at larger pore sizes, while the interaction with pore walls becomes the dominant factor at our smallest pore diameter. Deviation from the trends predicted by the Renkin equation [4] indicates that the interaction with the pore wall is not a just simple steric one but is in part dependent on the specific features of the molecules explored.

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Cooperative Adsorption and Gas Separations in Metal-Organic Frameworks

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Julia Oktawiec,[1] Lucy Darago,[1] Tomče Runčevski,[1] Jeffrey Martell,[1] Dianne Xiao,[1] Thomas McDonald,[1]
Jarad Mason,[1] Eric Bloch,[1] Zoey Herm,[1] Benjamin Keitz,[1] Brian Wiers,[1] Wendy Queen,[1,3] Stephen Geier,[1]
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Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications. In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for use as solid adsorbents in post- and pre-combustion CO_2 capture, and for the separation of O_2 from air, as required for oxy-fuel combustion. In particular, MOFs with diamine-functionalized metal sites are demonstrated to operate via an unprecedented cooperative insertion mechanism, leading to high selectivities and working capacities for the adsorption of CO_2 over N_2 under flue gas conditions.[1] Multicomponent adsorption measurements further show these compounds to be effective in the presence of water,[2] while calorimetry and temperature swing cycling data reveal low regeneration temperatures compared to aqueous amine solutions.[3,4] MOFs with redox-active coordinatively-unsaturated metal centers, such as the Fe^{2+} sites in Fe_2(dobdc) ($dobdc^{4-}$ = 2,5-dioxido-1,4- benzenedicarboxylate) allow the selective adsorption of O_2 over N_2 via an electron transfer mechanism.[5] The same material is demonstrated to be effective at 45 °C for the fractionation of mixtures of C1 and C2 hydrocarbons, and for the high-purity separation of ethylene/ethane and propylene/propane mixtures.[6] In addition, it will be shown that certain structural features possible within MOFs, but not in zeolites, can enable the fractionation of hexane isomers according to the degree of branching or octane number.[7] Finally, a new spin transition mechanism will be elaborated as a means of achieving cooperative CO adsorption.[8]

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Experimentally-Validated High-Throughput Computational Screening of Metal-Organic Frameworks for Neon and Nitrogen Adsorption Storage

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In 2020 the European space agency will launch a new earth observation satellite, which requires, among other features, a vibration-free cold finger continuously thermalized at 40 K. Following a call for bids, the design and manufacturing of the vibration-free cryocooler (VFC) was commissioned to a Portuguese consortium involving Active Space Technologies, the cryolab of LibPhys-UNL, and the laboratory of adsorption technology and process engineering at LAQV@REQUIMTE. The VFC is based on a cascade of adsorption pumps involving neon (Ne) and nitrogen (N_2) adsorption storage.

To address this challenging problem we have performed an extensive computational screening of metal organics frameworks (MOFs) and zeolites extracted from the Cambridge Structural Database (CSD) [1]. The CSD contains thousands of MOFs [2], yet most of these have never been tested for Ne or N_2 storage. An advantage of the proposed approach is that it relies on existing compounds rather than on hypothetical materials that may prove difficult to synthesize. (Nevertheless, achieving high neon capacities in known compounds still requires the synthesis of stable, solvent-free versions of these materials, a feat that is not always straightforward.)

To facilitate a computational assessment of these properties, we used data mining and structural routines to identify, “cleanup,” and rapidly characterize MOFs within the CSD [3]. For the potential candidates identified this survey their adsorption capacities were predicted by GCMC simulation for the sets of conditions of the vibration-free cryocooler. For Ne the charge pressure was 16 bar and temperatures between 130 and 180 K; the desorption pressure was up to 150 bar at 500 K. For N_2 the charge pressure was between 0.5 and 1 bar at temperatures between 160 and 180 K and the desorption step was at 500 K and pressures between 100 and 150 bar.

The best MOF materials were validated experimentally by successfully comparing fully predictive molecular simulation results with experimental adsorption isotherms for Ne and N_2. The predictions obtained by molecular simulation agree well with the experimental data.

Exploiting Diffusion Barrier and Chemical Affinity of Metal-Organic Frameworks for Efficient Hydrogen Isotope Separation

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Highly pure deuterium is an irreplaceable raw material for both industrial and scientific research, thus, the isolation of deuterium from nearly physicochemically identical isotopic mixtures is an important challenge in modern separation technology. Herein, we report a highly effective isotope separation system based on metal-organic frameworks (MOFs) via a simple post-modification strategy exhibiting the highest D2 over H2 selectivity (~26 at 77 K) of any system to date.

The essence of our approach toward the development of highly effective hydrogen isotope separation systems is the implementation of two quantum-sieving effects, kinetic quantum sieving (KQS) and chemical affinity quantum sieving (CAQS) in one system. For this purpose, MOF-74-Ni, having a high density of strong adsorption sites, which provide the CAQS effect, was chosen as a host material. Simultaneously, imidazole molecules are introduced into the 1D channel of MOF-74-Ni as a diffusion barrier, effectively reducing the aperture size and repeatedly blocking H2 diffusion, resulting in the KQS effect. This work is not only the first attempt to implement two quantum sieving effects, KQS and CAQS, in one system but also provides experimental validation of this system as a practical strategy for industrial applications.

Binary Adsorption of CO_2 and Water on UiO-66 MOF

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Metal organic frameworks are frequently examined as potential solutions to complex gas phase separations problems. In many cases, the gas phase adsorption properties of these materials are quantified using single component gas adsorption isotherms and breakthrough experiments. In adsorption separations, however, it is common that the adsorbent participates in a multicomponent adsorption event. In the literature there is a general absence of multicomponent adsorption data with most data predicted via the ideal adsorbed solution theory or molecular simulations. Therefore, in this work, binary adsorption data of CO_2 and water on UiO-66 were measured experimentally using a volumetric method at three different temperatures and at three different water loadings. Molecular simulations and ideal adsorbed solution theory calculations were also completed and the results of the simulations and the experiments compared. The data in this work can be used to examine the applicability of the ideal adsorbed solution theory to metal organic frameworks and can be used to validate molecular simulations of binary adsorption events.

CPM8 | POSTER ABSTRACT

FUNDING OPPORTUNITIES

CHARACTERIZATION OF PORE STRUCTURE AND CONFINED FLUIDS

Funding Opportunities at NSF's CBET division: Process Systems Cluster

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This interactive poster session will discuss funding opportunities in the National Science Foundation's Division of Chemical, Bioengineering, Environmental, and Transport Systems (CBET), with a focus on the Process Systems Cluster. The Process Systems Cluster includes four programs, including (1) Process Separations, (2) Catalysis, (3) Energy for Sustainability, and (4) Process Systems, Reaction Engineering, and Molecular Thermodynamics. The cluster's programs stress fundamental hypothesis-driven research for novel materials, processes, and/or tools that seek to improve the throughput, resource efficiency or process intensification of chemical conversion processes. Focus in on fundamental understanding emphasizing molecular-level engineering to link to understanding of performance at the process/system level. The Process Separations program supports research that furthers a fundamental understanding of the interfacial, transport, and thermodynamic behavior of multiphase chemical systems. A particular focus area is the design of scalable mass separating agents and/or a mechanistic understanding of the interfacial thermodynamics and transport phenomena that relate to purification of gases, chemicals, or water.

Characterization of Nuclear Concretes: Effect of thermal stress up to 1000°C

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An experimental study is carried out to characterize the alteration of siliceous (SC) and the sandlime (SLC) concretes under thermal stress. The microstructure, porosity, mass loss and specific surface area of both concretes are investigated in a temperature domain ranging from room temperature up to 1000 °C. The study of the thermal degradation of cement paste, aggregates and concretes was carried out using the thermo-gravimetric analysis. Mercury Intrusion Porosimetry was further applied to access to their porous structure. Samples consist in either monoliths or disaggregated concretes. When compared to SC, SLC samples show greater mass losses when exposed to temperatures higher than 700°C since much more gas would be produced from the decomposition process of calcium carbonate into quicklime and carbon dioxide [1]; [2]; [3]. Moreover, their porosity turns out to be twice larger than that of SC. SC and SLC are representative of French nuclear power plants. This work is therefore expected to bring new insights in the damages induced in their structure when in contact with molten metallic materials. This problem is of first importance for the understanding of the last phase of nuclear reactor accidents [4] [5].

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Characterisation of Polymer-based Composites with Enhanced Microporosity for Gas Storage

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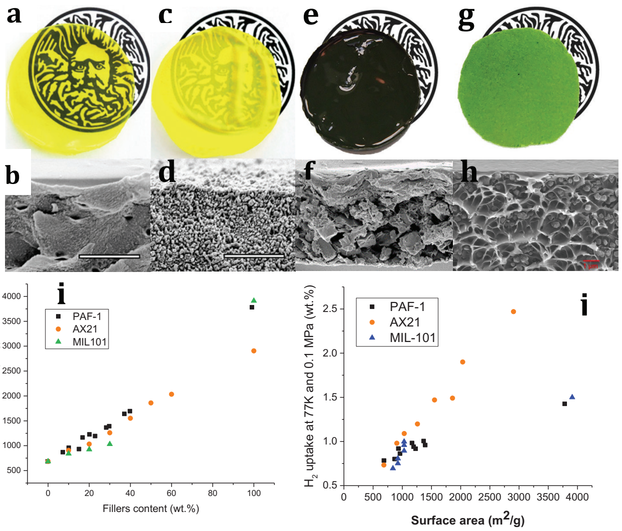

Figure 1. (a, c, e, g) Photographs of pure PIM-1, PIM-1/PAF-1, PIM-1/AX-21 and PIM-1/MIL-101 films; (b, d, f, h) SEM images of pure PIM-1 film, PIM-1/PAF-1, PIM-1/AX-21 and PIM-1/MIL-101 films; (i) BET surface area of PIM-1 composite films as a function of the weight fraction of the fillers; (j) H_2 uptake at 0.1 MPa and 77 K for PIM-1 composite films as a function of BET surface area.

A study on the functionalisation and characterisation of composite membranes (PIM-CMs) based on polymers of intrinsic microporosity (PIMs) with an application to gas storage is discussed. PIM-1 possesses relatively high surface area and microporosity because of its rigid ladder-like polymer backbone that prevents efficient chain packing[1]. PIM-1 can be processed into robust free-standing films using solvent-based techniques, and thus offers great potential for incorporation as liners inside high-pressure storage tanks to enhance their storage performance[2]. Here, a series of composite membranes with PIM-1 and selected porous fillers are fabricated by solvent casting. The selected porous fillers with extra-high surface area are the polyaromatic framework PAF-1[3], the metal-organic framework MIL-101 and activated carbon AX21. The PIM-CMs were characterised by thermogravimetric analysis (TGA), contact angle testing, scanning electron microscopy (SEM), and surface area and porosity analysis. The CO_2 uptake and H_2 adsorption properties were measured via high-pressure gravimetric and volumetric measurement, respectively. Incorporating porous fillers into PIM-1 endows the resultant composites with outstanding H_2 and CO_2 storage capacities. The synthesized composite membranes are stable and processable, and possess enhanced microporosity. The effects of fillers on the surface area and sorption capacity were also investigated. It was demonstrated that the surface area and porosity of the composite membranes play a key role in their hydrogen storage properties. These studies open the door to polymer-based porous composites for various applications.

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Absorption Artifacts upon Analysis of Organic Porous Materials with N2 Adsorption

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N2 adsorption analysis is a well-established method for determining specific surface areas and pore size distributions of mesoporous materials not only in research but also in quality control. The latter is supported by the fact that national and international standards exists to provide reproducible and comparable technical data, e.g. [1]. However, the method is not supposed to be applied for materials that significantly absorb nitrogen at the analysis temperature of 77 K. While it is well expected that organic samples, such as porous resins or foams, absorb significant amounts of gases and vapors at ambient conditions it is often assumed that solubility is highly reduced at cryogenic temperatures.

Using a sol-gel derived organic (resorcinol-formaldehyde (RF) based) model system with systematically varied mean meso- and macropore size [2], we identified significant absorption effects during nitrogen adsorption analysis: The evaluation of the isotherms delivered specific surface areas that were significantly different from the values estimated from the particles sizes (from SEM) or data derived from small angle X-ray scattering. Furthermore, we found indications, that not only was absorption largely contributing to the apparent adsorption isotherm, but kinetic effects (diffusion into the non-porous backbone) also controlled the amount actually absorbed. Thus, it is not possible to use nitrogen adsorption analysis for the characterization of RF based systems. So far it is not clear which other organic materials are similarly affected by absorption contributions.

To provide an alternative approach, we analyzed the above mentioned porous organic materials with Ar adsorption at 87 K, as well as with other probe molecules such as methane, butane and sulfurhexafluoride. We discuss the differences between these different adsorption data and give first recommendations for the analysis of porous organic materials.

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Pore size distribution from non-local density functional theory: Evaluation of adsorption-isotherm data fluctuations

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Models based on Statistics thermodynamics showed good results on representing the behavior of confined fluids, when compared with those based on Kelvin equation, with the highlight for methods based on density functional theory (DFT). These methods show accuracy like molecular simulation[1], but with less computational effort. For this reason, it is convenient to use DFT for porous material characterization. However, there are still doubts about the unicity and validity of the results for amorphous materials at the literature. This study evaluates the effects of the fluctuations observed in adsorption isotherms data on the recovery pore size distribution (PSD), considering an idealized material with micro and mesopores. The characterization was made by doing the deconvolution of the adsorption integral equation (AIE)[1], using lognormal distribution[2] representing the volume fraction distribution of the material pores. We built a kernel consisting of individuals' adsorption isotherms, applying non-local density functional theory to simulate the behavior of the fluid inside a slit-like pore[1]. The fluid considered here was argon at 87,4K[1] on slit pores of graphite. In order to observe how the possible experimental errors could effect on PSD analysis, two global isotherms were built by the convolution of the kernel with two different idealized PSD's, one with a unimodal and the other with a bimodal shape. To represent disturbed experimental isotherms, fluctuations with three different magnitudes were imposed on both global isotherms. The simulation of low, medium and high disturbed systems consisted of applying fluctuations of 1%, 5%, and 15% on the global isotherms generated. The disturbed global isotherms were used in the PSD recovering procedure in order to verify the capacity of the method to present, as a result, the PSD applied to generate the global isotherm. Results obtained here suggest that for low errors (1%) the method successfully recovered, all PSD. For systems that have fluctuation equal or greater than 5% it is possible to observe false positive results. The false positive results consisted on distributions that successfully fitted the adsorption data but presented a different shape when compared with the original idealized PSD used to generate the global isotherm. As an example, the global isotherm, with 5% disturbance, built with the unimodal idealized PSD, presented, after the recovery procedure, a bimodal PSD shape, when a sum of two lognormal was applied as a function of volume fraction distribution on the AIE. Results obtained here suggest high correlation between isotherm data fluctuations with the recovered PSD.

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How dense is the gas confined in nanopores?

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It is well know that the properties of nano-objects differ from those of their macroscopic analogs. Any system of nanometric size shows characteristics that strongly depend on its size and geometric form. It is mainly because the major part of atoms (or molecules) of nano-volume are located at the object surface and their cohesive energy is smaller than for the atoms in the bulk. As a consequence, the density of the nanoobjects is not homogeneous, and may decrease close to the object boundary. Here we show that when a fluid is confined in nano-volume, delimited by non-interacting pore walls, its density is on average smaller than the bulk density. The heterogeneous distribution of fluid density results from the nano-confinement, and progressively weakens when the pore size increases: it disappears for pores larger than 5 nm. On the other side, the fluid density approaches the ideal gas values in the limit of very small pores. This effect should be distinguished from the well know heterogeneity of density of fluids **adsorbed** in nanopores, driven by the difference between the strength of fluid-fluid and fluid-pore wall interactions. The reported observation has non-trivial influence on evaluation of excess/total adsorption in nanopores, as these two quantities are calculated assuming the known – and homogeneous – bulk density of gas in the pore. Additionally, the gas density in the pores depends on the definition of the pore volume which is neither straightforward nor unique. We analyze this phenomenon on an example of five gases: H_2, CH_4, the two intensively studied energy vectors, and N_2, Ar, and Kr, commonly used for characterization of porous structures. Two model pore geometries with not adsorbing soft walls are analyzed (slit-shaped and cylindrical). For H_2, the distributions of densities of gas confined in adsorbing and not adsorbing pores are compared and commented.

Gas Adsorption Studies on Shales and Gas-In-Place Calculations

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Recent progress in extraction techniques has propelled shale gas production; however, these processes remain largely inefficient. This stems from the lack of understanding of the effect of confinement on the fluids in the shale formations, which have nanometric pores, very low permeability and porosity. While primary methods of recovery provide suitable initial production rates, enhanced means of recovery using CO_2 injection [1] may be required to sustain them.

In shale, natural gas (a mixture of methane and ethane) is held freely in pores and fractures as well as adsorbed within the micropores of the organic matter [2] and clay minerals. As such, gas adsorption can be used to provide estimates for the Gas-In-Place (GIP) at subsurface conditions, but also as a tool for material characterisation by providing insights into the complex pore structure of shale. This investigation aims at (i) quantifying gas adsorption within shale, (ii) resolving the contribution of both the organic matter and clay to gas storage and (iii) assessing the pore space properties of shale.

Carbon dioxide (CO_2) and methane (CH_4) adsorption isotherms have been measured using a Rubotherm Magnetic Suspension Balance over a wide range of conditions, i.e. temperatures in the range 283-353K and in the pressure range of 0-300 bar. A selection of shale samples from the Bowland formation in the UK has been used and results are compared to data measured at the same conditions on a mesoporous carbon that is used as an analogue for the organic matter in shale. Estimates for the GIP and CO_2 storage capacity of the shales are obtained and compare well with those for key shale plays in the United States. Notably, the organic content of the shale can be used to scale adsorption isotherms measured on the mesoporous carbon, thus confirming that (i) shales are largely mesoporous and that (ii) organics play an important role in driving adsorption in shale. Moreover, shale shows significant selectivity towards CO_2 as compared to CH_4, thus providing an opportunity to exploit the adsorption/desorption process to further enhance gas production.

The shale samples are also characterised by low-pressure adsorption with N_2 at 77K and CO_2 at 273K and 298K to assess relevant structural parameters. The results confirm the observations from the supercritical adsorption experiments and are used to determine useful guidelines with regards to the effect of the shale composition (i.e. clay and organic content) on properties such as specific surface area, pore volume and pore size distribution.

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Artificial opals as a model of a shale rock: study of nanoconfined oil combustion

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The shale revolution in petroleum industry started in the USA and resulting in enhanced production of gas and oil from shale deposits, awakened increasing interest to studies of fluids behavior in a fine porous media. At the moment the influence of micro- and nanoconfinement on physical properties of hydrocarbons is well described phenomenon in a scientific literature [1-3]. The general conclusion from these studies is that confinement influences on both thermodynamics and kinetics of physical processes.

Unlike physical processes the influence of confinement on chemical reactions is a rare subject of research. In our study we applied artificial opals as a convenient model porous media to study kinetics of confined oil combustion. The choosing of synthetic opals, as a model porous medium, is related to their unique properties [4], which are: the regularity of pore network, the possibility of variation of the pore size distribution, constant porosity, high diffusion permeability, chemical inertness.

In our study we synthesized artificial opal samples and for the first time investigated their morphological and textural properties by means of SEM and nitrogen porosimetry. We also showed parameters of model porous media influence on kinetics of oil combustion.

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Determination of microstructural characteristics of advanced biocompatible nanofibrous membranes

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Biocompatible nanofibrous mats and membranes have attracted much attention in the last decade owing to their potential utilizing in a broad range of medical applications since the nanoscale is the typical scale for a life (e.g. globular proteins or DNA strains) related directly to human body. Therefore, advanced biocompatible and biodegradable nanofibrous materials can be utilized as bone tissue engineering [1], wound dressing, artificial organ, tissue templates, prostheses or drug delivery [2].

The proposed study aims to describe microstructural characteristics (both texture and transport parameters) of biocompatible nanofibrous membranes based on gelatin and chitosan prepared by electrospinning technique. Both materials represent a new class of biomedical nanomaterials with the typical disordered porous structure. The standard methods of texture analysis including the physical adsorption of inert gases, the high-pressure mercury porosimetry and the helium pycnometry were utilized for determination of the basic texture characteristics of the tested electrospun samples. Relevant transport characteristics were evaluated based on the isothermal steady-state regime of the gas transport measurements including the counter-current diffusion (carried out both in Graham's and Wicke-Kallenbach diffusion cells) and the isothermal quasi-stationary gas permeation (performed in permeation cell). Due to the prevailing macroporosity of the electrospun nanofibrous membranes, the evaluated transport parameters from the diffusion transport measurements reflect the gas transport mechanism taking place predominantly in the continuum regime. On the other hand, the gas permeation transport directly measured in the permeation cell carried out in the Knudsen regime predominantly. The accuracy of the transport parameters was judged based on the computed 95% confidence regions. It was confirmed that the confidence region shapes of the optimized transport parameters are intimately connected with the prevailing mass transport mechanism (Knudsen versus molecular or viscous flow).

The study has shown that mapping between the comprehensive knowledge of microstructural properties of the biocompatible electrospun membranes and their application properties is important contribution to the final product design.

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Morphology of living pore structure in microporous polypropylene film

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Microporous polypropylene film with living pore has been prepared by blown film extrusion. The commercial silica was prepared through melt-compounding processing and introduced into polypropylene. The effect of silica addition on water vapor permeability of polypropylene film was determined. It was found that the role of living pore which seems like stomata enhanced the water vapor permeability under negative pressure. The morphology and behavior of living pore were investigated by using in-situ tensile testing in scanning electron microscope (SEM). It was revealed that the applied force exhibited the formation of interstitial space between silica and polypropylene matrix. The porosity, pore size and pore size distribution were presented. Their mechanical properties in machine direction (MD) and transverse direction (TD) were evaluated. The relationship between drawing ratio and pore size was also observed.

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Use of Adsorbate Wetting Differences for Structural Characterization

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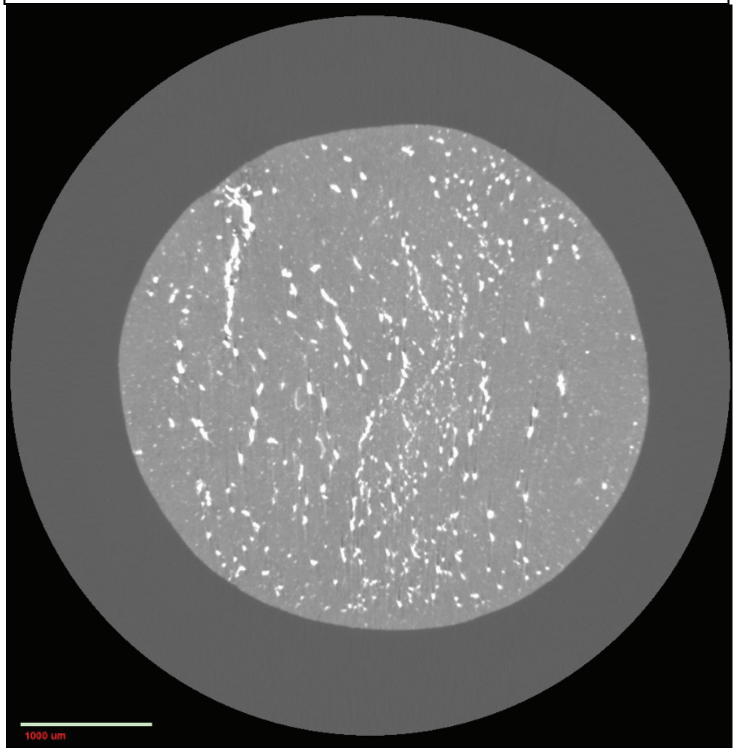
This work has demonstrated that the supposedly non-specific adsorbates, nitrogen and argon, will wet the surface of metallic mercury differently, and how this effect can be used in integrated gas sorption and mercury porosimetry experiments to obtain additional structural information, such as on pore inter-connectivity/juxtaposition. In the integrated experiments, the location of the entrapped mercury, in terms of distribution of filled pores, could be deduced from the porosimetry curves themselves and/or from the difference in amount adsorbed for the argon isotherms before and after mercury entrapment. The identity of pores neighbouring those filled by entrapped mercury can be deduced from the difference between argon and nitrogen isotherms. The impact of the new metallic surfaces on capillary condensation in these neighbouring pores can be derived from the nitrogen isotherms. For example, in a disordered but model pore system, where through-cylindrical pores were turned into dead-end pores by entrapment of mercury in other pores adjoining at one end, it was found that nitrogen would wet the new metal surface, while argon would not. This was determined since the original capillary condensation pressure for nitrogen in the pore was shifted to lower pressure, while that for argon was not. Hence, use of both argon and nitrogen in integrated experiments enabled the characteristic geometry of particular pores that determined sorption behaviour could be explicitly known even for disordered pore networks. This effect has been used to validate the overall hierarchical structure of a catalyst support pellet and determine the specific size distribution of the particular mesopores that open off macropores added to provide greater network accessibility. While the macropore network could easily be mapped by computerised X-ray tomography (CXT) (see Figure 1), the mesopores emptying off these macropores lay below the imaging resolution, but the new technique made this set of pores specifically detectable and measurable. The model for the pore network thereby obtained has also been validated by NMR cryoporometry and gas sorption scanning curves.

Fig. 1. CXT image of mercury entrapped in macroporosity of catalyst support pellet



Pore Network Analysis: Interpretation of Hysteresis Scanning Measurements

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Hysteresis scanning allows one to obtain detailed and complementary information about the underlying adsorption mechanism (desorption, cavitation, and/or pore blocking) and corresponding pore network characteristics such as pore connectivity and pore shape. After the measurement of the initial (boundary) curve, one measures subsequent adsorption/desorption cycles within the relative pressure range where hysteresis occurs by re-measuring the adsorption branch only up to a relative pressure associated with partial filling of the pore network. Hysteresis scanning curves observed for materials with independent cylindrical pore networks mimic the shape of the initial boundary curve, while disordered pore networks, with pore blocking and percolation effects, have hysteresis scans with a different shape. In the case of cavitation, scanning curves intersect horizontally with the boundary curve, similar to the case of independent pores, as cavitation is also independent of the state of the fluid in neighboring pores. Hysteresis scanning has been applied to three-dimensionally ordered mesoporous carbons [1] as well as to hierarchical zeolites [2] and methods based on molecular simulation have been suggested for a quantitative description of scanning curves [3]. However, there are still many challenges associated with the interpretation of hysteresis scanning curves. Within this context, we investigate the effects of pore network structure and surface chemistry on hysteresis scanning curves, i.e. we have performed systematic scanning hysteresis experiments with adsorptives such as N2, Ar (77,87 K,) and water (at 293, 98K) on nanoporous materials exhibiting a well-defined, ordered, pore structure, such as MCM-41, PMOs, and CMK-carbons.

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Thermodynamic studies on the phase behavior of water within periodic mesoporous organosilicas (PMOs) with different surface polarities

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Water is the precondition for life on earth the way we know it. One reason among others is that water can be found under various conditions in all three states of matter. In many cases these conditions are determined by the interaction with surfaces or the confinement in nanopores. Well defined host structures are needed to study the phase behavior of confined water. M41S silica host structures are ideal candidates due to their ordered monomodal cylindrical pore structure and tunable pore size in the interesting range of 2-6 nm. [1] In addition to the geometrical confinement it is also important to probe the influence of the surface chemistry on the phase behavior of a pore fluid. Periodic mesoporous organosilicas (PMOs) are ideal candidates because of their same pore structure but different adjustable surface polarities compared to pristine M41S silicas. [2,3]

Here different mesoporous silicas and PMOs with a MCM-41 type pore structure and narrow pore size distributions were synthesized using various cationic surfactants of different chain lengths. In case of PMOs precursors of the type $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ with R = ethane-, benzene-, biphenyl- or divinylaniline-bridge were used to introduce hydrophobicity or hydrophilicity into the pore walls. In case of the aromatic moieties materials with a modulated surface polarity were synthesized, too.

Thermodynamic properties of water confined within the nanopores were studied by differential scanning calorimetric (DSC). These measurements revealed that the suppression of the melting and freezing points is not only strongly depending on the pore size of the material, but also on the surface chemistry. In addition, multidimensional solid-state NMR spectroscopy could show that the molecular mobility and the spatial arrangement of the water within PMOs with aromatic bridging units are determined by the modulation of the surface polarity [4].

To learn more about the overall polarity and wettability of the pore walls water vapor sorption measurements were carried out using silicas and PMOs with the same pore size. There is a clear trend to shift the pore condensation step to higher relative pressures if a non-functionalized organic moiety becomes larger and therefore more hydrophobic. But in case of the divinylaniline-PMO the shift and therefore its polarity is similar to pristine MCM-41 silica which is probably caused by the primary amine group which allows the formation of hydrogen bonds to the inner pore water molecules. In order to get more insights into the pore adsorption and desorption mechanism water vapor sorption measurements were also carried out at different temperatures (298, 308, and 318 K).

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Textural Characterization of Shale Nanostructure

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Nanostructure characterization of shales has received tremendous interest in recent years and aids in the understanding of how gases (and in what volume) are stored and permeate/transport through a shale formation. Of particular interest is also how the different components of shale (clay, kerogen, mineral, total organic content, etc) contribute to the nanostructure. The pore size range in shales spans from ultramicropores to macropores, so there is a need to combine several different techniques in order to determine the complete shale pore structure. Gas sorption (CO_2 at 273 K, N_2 at 77 K, Ar at 87 K) combined with Hg porosimetry gives a complete micro-, meso-, and macropore size distribution as well as total pore volume. Micro- and mesopore size distributions were obtained using state-of-the-art density functional theory (DFT) methods. Pore connectivity is explored through a detailed study of the hysteresis loops of the N_2 or Ar isotherms. Kerogen was isolated intact from the shale sample and studied independently to compare the porosity of the kerogen to the porosity of the shale. Finally, transport in shale and the isolated kerogen component was studied via experiments on a zero length column.

Pore size and porosity analysis of meso- and macroporous sol-gel based materials by using electroacoustics

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We present a novel method of determining porosity and pore size of meso- and macroporous materials by transmitting ultrasound pulses through a small sized samples saturated with a liquid (e.g. gels).
Propagation of ultrasound through a fully wetted porous materials generates an electric response called seismoelectric current [1-3]. The liquid and the porous body matrix are compressible at high ultrasound frequencies (MHz). However, their compressibilities are different, which leads to a relative phase motion causing charge displacement and thus an oscillating electric current. It is possible to measure this seismoelectric current with existing electroacoustic devices initially designed for characterizing liquid dispersions. We demonstrate here that it is possible to utilize such technique for porosity/pore size characterization as well.
The capability of the new, fast characterization technique is demonstrated for monolithic organic aerogels, but also for other meso-macroporous sol-gel materials over a wide range in pore size. The experimental data reveal that the method provides an alternative tool in particular for the gel precursors of aerogels that cannot be reliably characterized by established methods such as gas adsorption and mercury porosimetry as for most aerogels severe in situ deformation artefacts are observed [4-6]. Information about the porosity of these materials can be obtained in a simple way by measuring the experimentally determined ratio of the electrical conductivity of the porous material to the equilibrium conductivity of the media (supernate); using this data the porosity can be calculated by applying the well-known Maxwell-Wagner theory [2].
We compare the results obtained from electroacoustics with pore size from beam bending experiments (pore sizes < 200nm) [5] and indirect approaches on identical samples to validate the reliability of the method.

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CPM8 | POSTER PRESENTATION

MOLECULAR SIMULATIONS & MODELING

Molecular Insight on the Behavior of Carbon Dioxide within Zeolites

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Sorbents that efficiently separate carbon dioxide from multi-species gas streams must have high carbon dioxide selectivity. In addition, carbon dioxide mobility within the materials must not be limiting. Some zeolites exhibit both of these properties and thus are attractive options as sorbents.

This work presents studies of diffusion and adsorption of carbon dioxide and other relevant gases within zeolites. To investigate the influence of pore geometry on adsorption, selectivity, and diffusion we simulate the behavior of carbon dioxide, nitrogen and carbon dioxide/nitrogen mixtures within structurally different all-silica zeolites. We have shown that all materials adsorb carbon dioxide selectively and that diffusion is fast enough to enable practical applications. The qualitative behavior, however, depends greatly on the geometry of the different zeolites. The nature of our atomistic simulations allowed us to understand the microscopic causes of these differences and to further appreciate the role of Coulombic forces. Such forces are even more important when extra-framework cations are present.

In particular, cations can block diffusion through narrow channels within a zeolite. In some materials, carbon dioxide can diffuse while other gases cannot. We used atomistic simulations and Ab-Initio Molecular Dynamics to investigate carbon dioxide diffusion and cation gating in zeolite Na-RHO. Our results provide a detailed molecular description of this phenomenon.

Furthermore, given the crucial role of cation behavior within substituted zeolites, we also investigate cation mobility and its dependence on the nature of the material.

Molecular Simulation of CO_2 Adsorption for Pore Characterization

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Carbon dioxide has proven to be a suitable probe molecule to characterize microporous carbons due to its ability to be adsorbed at ambient temperatures, allowing for faster diffusion rates and penetration into narrowest micropores not normally accessible by cryogenic adsorbates. Until recently, the limit in resolution of CO_2 adsorption at 273 K was about 2 nm due to the high pressures (~35 bar) necessary to fill mesopores. However, recent advances in instrumentation have allowed measurements of CO_2 isotherms up to the saturation pressure. At 273 K, high pressure CO_2 experiments in micro-mesoporous carbons have shown that CO_2 isotherms are reversible and do not show hysteresis in the mesopore region. However, upon temperature reduction, the hysteresis phenomenon does occur. This feature has important implications on the application of theoretical methods for determining the pore size distribution (PSD) by CO_2 adsorption.

In this work, we investigate the influence of temperature on the adsorption of CO_2 with the goal of developing a reliable method capable of predicting the specifics of capillary condensation hysteresis; such method is then used to create kernels of adsorption isotherms to aid on the characterization of these materials. Using Grand Canonical Monte Carlo (GCMC) and the Gauge-cell method, theoretical adsorption isotherms are calculated in modeled carbon pores in the temperature range of 195 K to 273 K. The adsorbent is modeled using simple homogeneous slit and cylindrical shaped pores while an atomistic model represents the adsorbate. Comparison of simulated isotherms with experimental data on reference hierarchical carbons shows good agreement on the condensation/evaporation pressure and hysteresis width across all the temperatures in this study; PSDs are calculated for the reference materials by solving the adsorption integral equation.

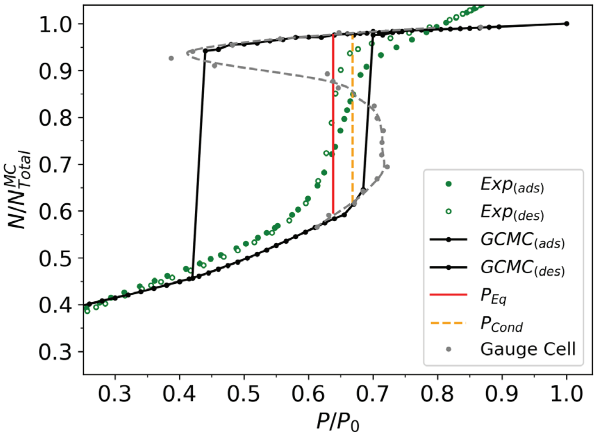

Fig 1. Comparison of experimental data of CMK-3 sample with simulated isotherms at 220 K.

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Pore Structure Characterization of MOF-based Materials by Gas Adsorption

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Adsorption of test adsorbates, such as N_2, Ar and CO_2, is the most practical method for pore structure characterization of MOF-based materials, which in many cases display composite hierarchical structures. The pore size distribution analysis is commonly based on conventional NLDFT or QSDFT methods developed for carbon and silica microporous solids. The kernels of references isotherms employed in these methods do not take into account the specifics of MOF pore morphologies, which differ significantly from one MOF family to another. In some cases, application of these methods provides reasonable agreement with the crystallographic pore dimensions, however, in many cases the discrepancies are striking. To remedy this situation, we develop dedicated kernels of reference "fingerprint" isotherms capable of distinguishing between different MOF structures and access the defects, inter-crystalline pores, and secondary micro-mesopore structures of binding materials. The fingerprint isotherms are built from MC simulated isotherms verified by experiments on ideal non-defective MOF crystals. The efficiency of the proposed approach is demonstrated by drawing on the example of Cu-BTC composites.

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Adsorption of hydrogen isotopes in the zeolite NaX: Experiments and simulations

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Among the different methods to separate hydrogen isotopes one is based on the physisorption at low temperature (below 100 K) where quantum effects induce a particular behavior. In the present work, we study the adsorption of single H2 and D2 on the zeolite NaX by combining experiments (manometry) from 30 to 150 K and molecular dynamics simulations at 40 and 77 K. Simulations also include the adsorption analysis for T2. Adsorption on NaX membranes is simulated and quantum corrections are introduced by using the well-known FeynmaneHibbs approach into the interaction potentials. Experimental adsorption isotherms are reproduced by using the Toth equation and it is shown that the adsorption capacity increases with the molecular weight of the isotopes. Isosteric enthalpies evidence a heterogeneous adsorption process with two type of hydrogen isotopes differently linked to the zeolitic structure. The calculated pair distribution functions at high loadings exhibit a liquid-like structuration in the supercages of NaX, which may explain the different adsorption capacities for H2, D2 and T2 and the heterogeneity of the adsorption process.

Compressibility of Nitrogen Adsorbed in Vycor Glass

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Nitrogen adsorption is one of the main characterization techniques for nanoporous materials; experimental adsorption isotherm provides the information on the BET surface area and pore size distribution (PSD) for a sample. Typically, adsorption isotherms are measured by volumetric or gravimetric methods [1], however, there could be alternative approaches. In particular, Warner and Beamish proposed to use ultrasound for this purpose [2]. They showed that the adsorption isotherm derived from ultrasonic measurements is fully consistent with the volumetric ones and applicable for calculation of the specific surface area.

Instead of using the ultrasonic measurements as an alternative, we suggest interpreting these data as complementary information. Knowing the adsorption isotherm from independent (e.g., volumetric) measurements allows one predicting the change of the elastic modulus of the adsorbed nitrogen from the measured change of ultrasonic velocity. We use the classical Gassmann equation [3], which has been recently adapted for nanoporous materials [4], to extract the shear and the longitudinal moduli of the adsorbed liquid nitrogen from the sound velocity data from [2]. We found that, similarly to bulk liquid nitrogen, the shear modulus of the adsorbed nitrogen is zero. However, the longitudinal modulus noticeably deviates from the bulk value and changes with the equilibrium vapor pressure.

In addition to analysis of the experimental data, we carried out a molecular simulation of nitrogen adsorption in silica pores of various sizes. The simulations employed Monte Carlo method in the grand canonical ensemble, which gives the isothermal compressibility of the adsorbed fluid from the fluctuations of the number of molecules in the pore [5]. The results of our simulations demonstrated a decent agreement with the experimental data from [2]. Moreover, they reveal a simple relation between the pore size and the compressibility of adsorbed nitrogen. This relation suggests that the ultrasonic experiments can be utilized for characterization of porous materials, providing information complementary to adsorption isotherms.

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Predictions of Solvation Pressure in Mesopores Based on Saam-Cole Theory

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Adsorption-induced deformation has been found to manifest in numerous natural and engineering processes, e.g., drying of concrete, water-actuated movement of non-living plant tissues, swelling of coal and shale, etc. [1]. The driving force for the deformation is solvation pressure – the pressure that a fluid adsorbed in a nanopore exerts on the pore walls. Solvation pressure can be calculated from the derivative of the grand potential of the adsorbed fluid, which in its own turn can be derived from the adsorption isotherm [2,3].

Adsorption isotherms of mesoporous materials can be calculated via various thermodynamic approaches, two of them are Derjaguin-Broekhoff-de Boer (DBdB) [4] and Cole-Saam (CS) models [5]. These models are based on similar thermodynamic equations to describe phase transitions in nanopores, considering the influence of the pore wall in the form of solid-fluid interaction potential. However, they use different simplifying assumptions. CS theory, in contrast to DBdB, takes into account the curvature influence on the potential, giving more rigorous predictions for the adsorption isotherms.

In this work we derived analytical expressions for solvation pressures in cylindrical and spherical pores based on CS theory and used these expressions to perform calculations of solvation pressure corresponding to adsorption of N_2 and Ar in silica pores. We compared our results with the calculations based on DBdB theory [3]. We showed, that while the predictions of CS and DBDB theory for isotherms for both geometries differ noticeably, the difference between the solvation pressure isotherms is less pronounced. This conclusion justifies application of either of the two macroscopic methods for predicting adsorption-induced deformation of mesoporous materials.

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A Universal Isotherm Model for Adsorption Uptake and Energy Distribution Design of Porous Heterogeneous Surface

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Based upon the adsorbate-adsorbent interactions due to pore size distribution and surface heterogeneity, as characterized by the adsorption isotherms, the adsorption phenomena has many industrial and environmental application. These adsorption isotherms are very important to define the information related to the equilibrium uptake of adsorbate-adsorbent pair. Due to presence of different energy distribution of adsorption sites, pore size distribution, surface area availability and surface heterogeneity, of each of the adsorbent-adsorbate pair, these isotherms are categorized into six types by the International Union of Pure and Applied Chemistry (IUPAC). Such pores occur naturally or can be chemically/thermally functionalized to form the desired heterogeneous surfaces with prescribed level of energy sites of assorted probabilities for vapor capture, resulting in a useful shape or form of these isotherms. So far in literature, there is no generalized adsorption isotherm model available that can define and predict the behavior of all of the six adsorption isotherm types. In this study, a universal adsorption isotherm model is developed based upon the energy distribution function of the available adsorption sites and the pore size. The proposed model is able to define all of the six adsorption isotherm characteristics, irrespective of their multi or mono layer formations and micro or meso-pore distribution. For modelling purposes, we introduce a fractional probability factor to define the fraction of the total surface coverage or the energy distribution, associated with each pore size or adsorbate layers of multi-layer formation. Unlike to conventional design methods of trial and error in configuring the sorption system based solely upon an isotherm shape, our model provides an insight to how the surface characteristics that are intrinsically linked to pore/cage dimensions, surface areas and pore-size distributions, surface-adsorbate charges, etc. In principle, these surface parameters can be readily modified or functionalized by material scientists or chemists. Hence, a dedicated porous adsorbent- adsorbate pair can now be designed or tailored, by a chemist or material scientist using established surface treatment techniques, to effect the mean and variance/deviation of desired surface energy distributions (EDFs) designed for a specific application.

Measuring and Modelling Sub- and Supercritical Gas Adsorption on Clays

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The injection of CO_2 into deep geological formations has attracted much attention as a technical solution towards reducing anthropogenic emissions of this greenhouse gas. Promising geological storage sites for CO_2 injection that meet the required storage capacity include deep saline aquifers and gas reservoirs where enhanced gas recovery processes may be implemented, such as coal seams or shale formations [1]. Clay minerals are ubiquitous in these targets and are major constituents of the cap rock seals above them. These minerals are characterised by the presence of micro- and mesopores, which results in a large surface area available for physical and chemical interactions with the surrounding fluids. Of particular interest to this study is the sorption behaviour of CO_2 and CH_4 on clay minerals that leads to the trapping of these gases in the porous structure at liquid-like densities. For the geological storage of CO_2, gas adsorption on clays can have several implications including (i) an increase of storage capacity in reservoirs having large clay contents [1], (ii) an advance in storage safety by limiting gas diffusion through cap rock seals [2], and (iii) an enhancement of gas production from tight shale formations through an adsorption/desorption (CO_2/CH_4) process, as observed for deep coal seams [3]. Remarkably, the study of gas adsorption in clay minerals at high-pressures and temperatures is still at the early stage of investigation, despite its importance. The main reason for this is the intrinsic difficulty in performing the experiments and in describing the complex interactions between the gases and clays.

In this study, adsorption data of CO_2 and CH_4 on pure clay minerals – Na-montmorillonite (SWy-2) and illite-smectite mixture (ISCz-1) – have been measured using a Rubotherm magnetic suspension balance (Bochum, Germany) in the pressure range 0-25 MPa at varying temperatures 25-115°C. Cryogenic low-pressure N_2 adsorption experiments have been conducted on the samples to determine the microscopic properties, such as their pore size distributions, surface areas, and pore structure. The adsorption data on clay minerals are compared to that measured under similar conditions on reference materials with well-defined pore sizes, including mesoporous silica and mesoporous zeolites. To support the experimental observations, the measured adsorption isotherms are described using a so-called Lattice Density Functional Theory (LDFT) model [4] that uses the pore structure of the clays as an input parameter. We report here on the development of a novel workflow, whereby the cryogenic N_2 adsorption isotherms are first fitted by the LDFT to determine the relevant pore-size classes and pore geometry. The model is subsequently applied to describe the supercritical adsorption isotherm by using the solid-fluid interaction energy (fluid-dependent, but temperature-independent) as a fitting parameter. As such, the modelling approach is more rigorous, has predictive capability, and represents a significant departure from conventional empirical approaches that use Langmuir- or BET-type of models.

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Comprehensive Modeling of Capillary Condensation/Evaporation in Open-Ended Nanopores

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The understanding of capillary condensation and evaporation in open-ended cylindrical nanopores is vital to characterize the porous materials. Many studies have revealed that capillary evaporation is the equilibrium phase transition, and several thermodynamic models have been proposed to predict the capillary evaporation pressure P_{evap}. On the other hand, capillary condensation is an activated process with nucleation; thus, the conventional thermodynamic models cannot estimate the capillary condensation pressure P_{cond}. In this study, the vapor-liquid phase transition in open-ended nanopores is modeled not only thermodynamically but also kinetically, to provide reasonable estimates of both P_{cond} and P_{evap}.

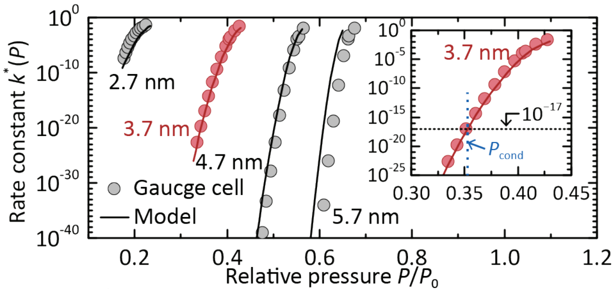

Fig. 1 $k^*(P)$ for various pore sizes

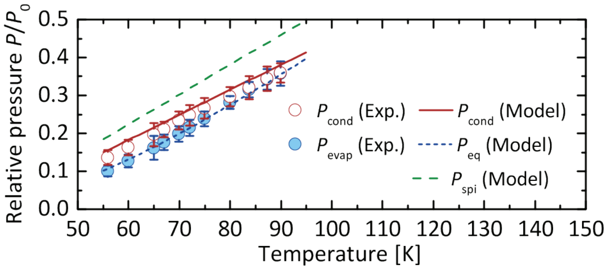

Fig. 2 Temperature dependences of P_{cond} and P_{evap} of argon for MCM-41 (Pore dia. 3.8 nm)

We first calculated a free energy change during the capillary condensation process, in analogy with the classical nucleation theory. In this calculation, the second-order curvature correction to the surface tension of the vapor-liquid interface was taken into account, which is the difference from the conventional models. The equilibrium phase transition pressure P_{eq} was determined as the pressure where the free energies before/after condensation are equal (thermodynamic model). Moreover, we evaluated a dimensionless rate constant of capillary condensation $k^*(P)$ by applying the transition state theory to the calculated free energy landscape (kinetic model).

Fig. 1 shows $k^*(P)$ for argon adsorption on cylindrical nanopores with various pore sizes, together with those calculated in our previous molecular simulation study [1]. The comparison demonstrates that the two approaches are in good agreement for all studied pores, which verifies the kinetic model. In our previous study [1], we found that capillary condensation occurs when $k^*(P)$ reaches the critical rate constant $k^*_{\mathrm{c}} = 10^{-17}$. Thus, as shown in the inset of Figure 1, we can estimate P_{cond} by applying the finding to the $k^*(P)$ curve obtained from the kinetic model ($k^*(P_{\mathrm{cond}}) = 10^{-17}$).

Fig. 2 shows the temperature dependences of the experimental P_{cond} and P_{evap} of argon for the MCM-41 material (pore dia. 3.8 nm). The graph demonstrates that P_{eq} values estimated from the thermodynamic model are coincided with the P_{evap} values. Moreover, even though the metastable limit (vapor-like spinodal) P_{spi} fails to reproduce P_{cond}, the kinetic model successfully predicts P_{cond}. Using the comprehensive models, we confirmed that the temperature dependences of P_{evap} and P_{cond} for different pore sizes (4.5 and 6.8 nm) are also successfully reproduced.

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Pore Size Distribution in Hierarchical Materials: Insights from Molecular Simulations

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Hierarchical materials, such as mesoporous zeolites, comprise of a distribution of pore sizes ranging from micropores (<2 nm) to mesopores (2–50 nm). Knowledge of pore size distribution is critical in designing and optimizing materials for various applications including, catalysis, separation, and gas storage and sequestration. Among the various available techniques for pore characterization, gas adsorption allows for determining a wide range of pore sizes in a non-destructive manner. Deducing the pore size distribution from the measured adsorption isotherms for argon, nitrogen, and/or carbon dioxide relies on theoretical procedures that utilize non-local density functional theory (NLDFT) or quenched-solid density functional theory (QSDFT) for the prediction of isotherms. These DFT predictions are limited to specific pore geometries (spherical, cylindrical, and slit pores) including DFT kernels consisting of hybrid pore geometries (e.g. assuming different pore geometries for micro-and mesopore range), and represent the pore walls either as uniform surfaces or incorporating some degree of heterogeneity using interaction parameters tailored to entire classes of adsorbents, such as carbons, silicas, and zeolites.

In this work, large-scale Monte Carlo simulations are carried out to probe the adsorption in hierarchical zeolites. An attempt is made to understand the dependence of adsorption on confinement in the mesopores of these zeolites. By investigating a large number of mesopore dimensions, a correlation between the capillary condensation pressure and the geometry of the pores is established. In addition an analysis of the differential loading is carried out and compared to the pore size distributions deduced from DFT.

Acknowledgements:
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Intrusion of water and electrolytes in hydrophobic soft porous crystals: some insights from molecular simulation

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Porous materials such as activated carbons, carbon nanotubes, zeolites and other open framework inorganic materials have been the subject of an intense research effort in the past two or three decades, owing to their practical importance in such processes as fluid separation, ion exchange, strategic gas storage, catalysis, biosensing and controlled drug delivery.

In 2001, Eroshenko *et al.*[1] started to explore an other application for these materials, namely energy storage and dissipation through the forced intrusion of a non wetting fluids these porous media. In terms of energy storage devices, a system displaying an intrusion–extrusion cycle without hysteresis can simply be termed as a ‘‘spring’’. A system with hysteresis is a ‘‘shock absorber’’ and an incomplete cycle in which water is retained in the porous framework upon pressure release can be called a ‘‘bumper’’ (see figure 1) [2]. The initial studies on intrusion used pure water as a non-wetting fluid, and high concentration electrolytes are now used too, giving the ability to tune the intrusion pressure using the osmotic pressure that arise between the external and intruded fluid[3].

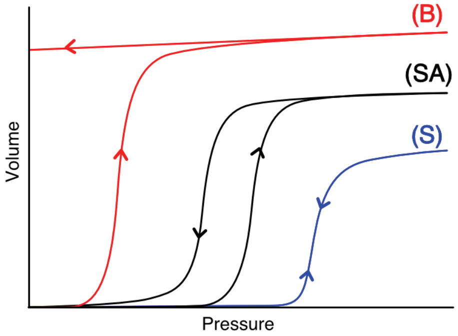

Fig 1: Typical intrusion-extrusion curves for spring (S), shock absorber (SA) and bumper (B) types material

We use multiple molecular simulation technics to gain atomic scale insights on the intrusion phenomena; from Monte Carlo simulation at the thermodynamic equilibrium, to molecular dynamics and metadynamics studies of the free energy landscape. We try to address the origin of the different behaviors during intrusion (from bumpers to springs). For the intrusion of electrolytes, we looked at the effects of different chemical species and concentration on the intrusion behavior.

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Computational Study of Vibrational Properties of ZIFs with SOD topology

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ZIFs are porous materials composed of tetrahedrally coordinated metal centers connected by imidazolate linkers. These materials have recently attracted scientific attention due to many possible applications such as gas storage gas storage and gas or liquid separation. Some of the materials from ZIF group possesses particularly interesting vibrational properties such as gate-opening mechanism in ZIF-8 [1] and ZIF-7 [2] (hence, they are referred as flexible ZIFs). ZIF-8 was previously studied with experimental and computational methods and it has been shown that the low-energy vibrations (<100 cm^{-1}) are responsible for the deformation processes such as gate-opening.

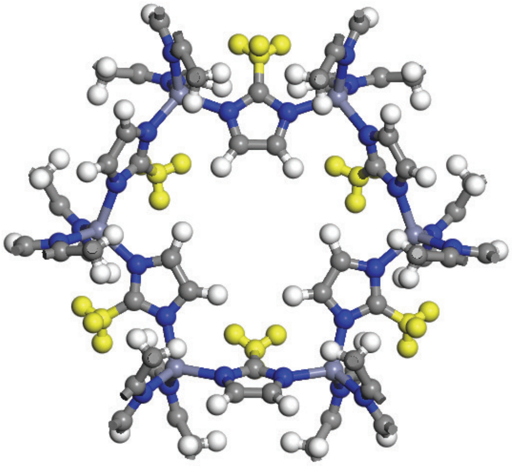

Figure 1. Part of the structure of ZIF-8 with highlighted methyl groups - possible substitution sites.

Our research was extended to other structures with the same SOD topology but (i) different metal ions in metallic centers (B and Li or Cu at the tetrahedrally coordinated positions, Co, Cd), (ii) different functionalization of imidazolate ring (–H, –NO_2, –H, -NH_2, –CHO) and (iii) different geometry (ZIF-7 and ZIF-9). We used density-functional theory in conjunction with the finite displacement method to predict the normal modes and visualize vibrations of the lattice. Results were used to determine how changes in composition or geometry affect the presence and frequency of the mode related to the gate opening mechanism. We show that there are several particularly interesting modes – one which is a symmetric distortion of the framework leading to opening of the pore (IR inactive due to its high symmetry) and a collection of IR active modes which might be related to asymmetric gate-opening. We claim that the frequency of the IR inactive "gate opening" mode is caused by the interactions between the linkers, therefore depending on attraction/repulsion between the attached functional groups. In contrast, the frequencies (and hence energies) of the IR active modes are sensitive and proportional to the mass of the linker.

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Influence of intermediate structures of MIL-53 on adsorption mechanism

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MIL-53 is a MOF porous structures which exhibits very pronounced flexibility. As a consequence, adsorption of CO_2 and water causes its reversible structural transformation, induced by the host-guest interactions. Here, we present detailed molecular modeling study of adsorption of CO_2, CH_4 and H_2O in the intermediate structures of the MOF. We use 20 intermediate structures, between the open pore one and the closed pore form of MIL-53, to study adsorption during the "breathing" of the MOF [1]. 18 intermediate structures were prepared using geometrical interpolation (Fig. 1) and they have been optimized using the DFT quantum calculations. Each structure is rigid and it represents an instantaneous non-equilibrium MOF configuration.

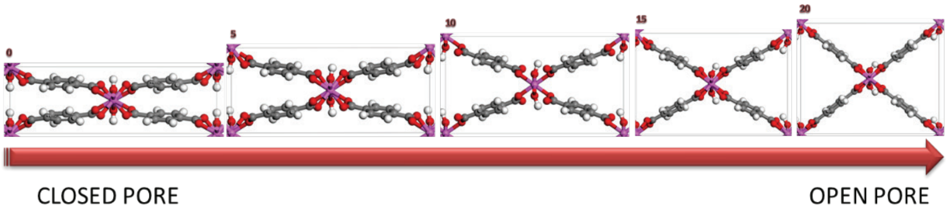

Figure 1. Intermediate structures of MIL-53(Al), as used in molecular simulations. 0 – closed pore structure, 1-19 – intermediate DFT optimized structures and 20 – open pore structure.

RASPA code is used for molecular simulation [2]. Grand Canonical Monte Carlo and Molecular Dynamic methods are applied to calculate isotherms of adsorption and diffusion coefficients at various temperatures. The simulated adsorption in the intermediate structures show differences in adsorption mechanism of CO_2, CH_4 and H_2O. The modeling of adsorption in the intermediate structures allows us to analyze the states which are not in equilibrium and are not accessible in conventional adsorption experiments. For better understanding of the interactions model applied during the process of adsorption, we compare our results with experimentally measured isotherms of adsorption.

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Disclosing adsorption mechanisms in Zr-based MOFs using a molecular modeling approach

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Metal-organic frameworks (MOFs) have become an important class of materials during the last decades. They consist of inorganic building units (IBUs) connected by organic molecules as linkers, resulting in a nanoporous framework. In dependence of the choice of metal atom and linker molecule, pore sizes, shapes, and other characteristics can be adjusted, leading to a wide range of applications like gas storage and separation, catalysis or biomedicine. With regard to the given application, Zr-based MOFs are of particular interest, due to their high chemical and thermal stability.[1]

UiO-66 is a well-known Zr-based MOF. The typical Zr-IBU is connected to each other by terephthalate to form a framework with fcu topology. Therefore, this MOF material exhibit two different types of pores, an octahedrally shaped one and a tetrahedrally shaped one.[2] The sizes of these pores have been given as 0.75 and 1.2 nm, respectively.[3] The utilization of larger linker molecules containing phenylene and ethylene units, a subclass of porous interpenetrated zirconium-organic frameworks (PIZOFs) can be accessed experimentally. These materials contain two-fold interpenetrated frameworks, with inherent small and large pores (0.6 and 1.9 nm).[3]

Here, we present results of both, experiments and Grand Canonical Monte Carlo (GCMC) simulations of gas adsorption of different adsorptives like Ar or N_2 in different chosen Zr-based MOFs to reveal the sorption mechanisms. Atoms of the frameworks are fixed during the simulation, while guest molecules are placed randomly within the structure. The simulations are carried out employing the universal force field (UFF) for the zirconium atoms and the DREIDING force field to describe energy contributions by the remaining framework. To make sure that the system is in equilibrium, $5 \cdot 10^6$ Monte Carlo steps for each state point are performed, followed by $5 \cdot 10^6$ production steps. Since some adsorptives exhibit quadrupole moments, the atomic charges must be considered. For this purpose, density functional theory (DFT) is used on representative clusters from the corresponding structures.[4]

In this work we present molecular models, showing sorption isotherms in good agreement with experimental data. Moreover, modeling investigations enable us to reveal the sorption mechanisms in detail.

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Heterogeneous multikernel analysis of carbon microstructure

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A heterogeneous multikernel of N2 adsorption isotherms for activated carbon characterization is developed on the basis of experimental insights from oxidative etching mechanism. By splitting the pore size distribution in 4 degree of etching, one obtains a detailed analysis of the development of porosity as the microstructure evolve with the burn-off, which is a fundamental information to design of the physical activation process by steam or CO2. The same kernel is able to differentiate between graphitized and non-graphitized surfaces. Previously studies had already demonstrated that heterogeneous surfaces [1-5] could be reliably used to probe the physical structure of the solid phase in carbons. We will demonstrate how an etched multikernel can be used to extract new data that allow the optimization of carbons obtained in the commercial processes of physical activation and how the use of such kernel can help enable a method of non-destructive characterization of defects in graphene-like materials [6]. Moreover this study supports the idea that multiple heterogeneous kernels are fundamental to narrow the gap between models and real materials.

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Conformal Sites Model for Adsorbed Films on Energetically Heterogeneous Surfaces

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Molecular simulations and theoretical analyses of thin films adsorbed onto solid surfaces or within narrow pores have usually treated the solid surfaces as atomically smooth and energetically homogeneous. Most surfaces, however, exhibit roughness through geometric curvature, variations of surface composition and chemical groups attached to the surfaces. Such oversimplification of the surfaces thus misses important features of adsorption, especially at low bulk pressure. In this research, a flexible conformal sites model, mapping a real interfacial system with an energetically heterogeneous surface onto a reference system with an energetically homogeneous surface, is developed. Grand canonical Monte Carlo simulation is used to explore the limits of applicability of this model to the prediction of adsorption isotherms. Preliminary simulation results show that our conformal sites theory is quite successful in reproducing the adsorption behavior in non-polar systems and in slightly heterogeneous polar systems. Due to the simplicity and accuracy of the theory, we anticipate this new method may be incorporated in the software of experimental instrument to study porous materials by taking advantage of the corresponding states theory.

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Heterogeneous surface models obtained by reactive molecular dynamics

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At the end of the 1990s, studies of heterogeneities in carbonaceous materials began to focus on the proposition of heterogeneous structures and their correlation with adsorptive properties [1-5]. In common, the heterogeneities of these models are obtained through semi-empirical methods by arbitrary criteria validated by indirect inferences from experimental results. Using reactive molecular dynamics, we obtained a solution for heterogeneous structure where no precondition is established in the process, only the underlying chemical phenomena. These new models reproduce the calorimetric data of the standard carbon BP280 and the Sterling 1500, superior to any other existing proposal. This solution incorporates the three classes of heterogeneities that are being studied separately (edges, amorphization and corrugations) representing a synthesis of the studies carried out up to now. We also have shown that this solution applies to the carbons spheron 1000 and LMA10. Extensive studies, which were previously limited due to the lack of reliable heterogeneous models, can now be performed, such as surface analysis made with more accurate isotherms kernel, impacts of heterogeneities in energy storage and CO_2 capture and characterization of graphene-based materials.

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Acknowledgements:

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NIST Data Resources for Cataloging Adsorption Measurements

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The National Institute of Standards and Technology (NIST), in cooperation with the Advanced Research Projects Agency–Energy (ARPA-E) of the U.S. Department of Energy, has developed several resources for cataloging adsorbent materials and curating data regarding adsorption of gases by those materials. These reference data products are intended to be used to disseminate data and properties of the cataloged adsorption systems for use by groups across disciplines and sectors, including industry, academia, instrument manufacturers, standards bodies, and government laboratories. One product is primarily a catalog of adsorption experiments, with an emphasis on the collection and presentation of measured adsorption isotherms. The second product is a registry of adsorbent materials, with a "crowd sourcing" module that allows users to propose new materials for the registry, suggest edits to material metadata, and propose merger of identical materials that may exist due to ambiguity in naming. Interested parties can access these tools for comparison with their own measurements, to test and calibrate equipment, or to screen adsorbents and adsorbates for desired behavior or properties. The data for adsorbent materials, adsorbate fluids, and their interactions are obtained from published scientific literature and measurements at participating laboratories, including the NIST Facility for Adsorbent Characterization and Testing. In this work, we present the web-based database of adsorption isotherms, an associated registry of adsorbent materials, and various software tools that exploit the extensive data set contained in these NIST data products. We also discuss the project's goals, both to advertise the new resource and to foster conversations that will improve the goals and future direction of the work so that it is a truly beneficial to the broad community studying adsorbent materials and those utilizing porous materials for end applications. We also discuss pitfalls encountered while gathering adsorption data from the scientific literature related to inconsistencies and common errors in data presentation. These difficulties, however, have also identified opportunities for standardizing the presentation of adsorption data, which could greatly aid comparisons of adsorption data from different laboratories as well as ease the inclusion of newly-measured adsorption data into the NIST database. Finally, we discuss other opportunities for improving the presentation and dissemination of adsorption data, including the introduction of a standard isotherm format, community submissions to the NIST database, and indexing/cataloging of adsorbent materials.

pyGAPS: A Python-based General Adsorption Processing Suite

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In this work we present an open-source and user-friendly python based framework for analysis, processing and storage of adsorption data.

While adsorption instruments commonly include professional-grade software which can perform a comprehensive analysis on the isotherms measured, bulk processing of adsorption data independent of source remains an endeavor. To enable high throughput experiment processing, as well as to lower the barrier of entry to adsorption characterization, a framework has been written in Python which can perform general isotherm processing, isotherm modelling, conversion from and to several popular formats as well as storage of measurements.

The code is based on tried and tested methods and models which can be applied on a variety of adsorbents and adsorbates and is written to be extensible and easy to work with. Furthermore, due to its open-source nature and permissive license, it can be used in both commercial and academic projects free of charge.

The framework offers features such as:

- Routine analysis such as BET surface area, t-plot, alpha-s method
- Pore size distribution calculations for mesopores (BJH, DH), micropores (HK) and DFT kernel fitting
- Isotherm modelling (Henry, Langmuir, DS/TS Langmuir, etc..)
- IAST predictions for binary adsorption (using a modified version of pyIAST [1])
- Isosteric heat of adsorption calculation
- Parsing to and from multiple formats such as Excel, CSV and JSON.
- An sqlite database backend for storing and retrieving data
- Simple but powerful methods for isotherm graphing and comparison
- Integration with either CoolProp [2] or REFPROP for fluid calculations

Source code can be found at https://github.com/pauliacomi/pyGAPS

Documentation can be found at https://pygaps.readthedocs.io/en/latest/

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CPM8 | POSTER PRESENTATION

ADVANCED MATERIALS: OXIDIC

Catalytic activity of desilicated and modified with Cu commercial ZSM-5 in environmental processes

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In the presented studies commercial ZSM-5 zeolite was desilicated using NaOH and NaOH/TPAOH (tetrapropylammonium hydroxide) mixtures and modified with Cu by ion-exchange method. An influence of TPAOH (TPA^+/OH^- ratio) and desilication conditions (temperature, time) on the catalytic activity in two important environmental processes NH_3-SCR (Selective Catalytic Reduction of NO with NH_3) and NH_3-SCO (Selective Catalytic Oxidation of NH_3) was investigated[1].

Nitrogen oxides, NO_x, emitted from diesel engines (the source of high NO_x emission) can be catalytically reduced to N_2 with the use of NH_3 (NH_3-SCR, also called $DeNO_x$ process). To avoid unreacted ammonia slip the second catalyst bed for selective ammonia oxidation to dinitrogen (NH_3-SCO process) should be installed downstream of the $DeNO_x$ converter. In this work one catalyst active in the both processes, which proceed in different temperature ranges (Fig. 1), was proposed.

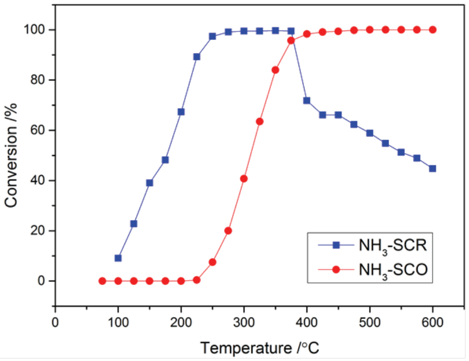

Fig.1. Comparison of NO and NH_3 conversions during the NH_3-SCR and NH_3-SCO processes over Cu-ZSM-5(meso)

Modification of ZSM-5 by desilication resulted in generation of mesoporosity with simultaneous decrease in microporosity and crystallinity and increase in surface acidity. Moreover, the applied modifications influenced reducibility of introduced Cu, what was probably responsible for the enhanced catalytic activity of the micro-mesoporous samples in NH_3-SCR and NH_3-SCO.

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Montmorillonites intercalated with SiO_2–Al_2O_3, SiO_2–TiO_2 and SiO_2–ZrO_2 pillars in the role off effective catalysts for methanol and ethanol dehydration

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Clay minerals are very promising raw materials for possible applications in various areas, including also catalysis. One of the most important method of clay minerals functionalisation for catalysis is based on surfactant-directed intercalation with silica pillars resulting in porous clay heterostructures (PCHs)[1]. This method of clay minerals modification results in materials with large surface area and porosity as well as high thermal and hydrothermal stability[2].

Dimethyl (DME) and diethyl (DEE) ethers are promising, environmentally friendly and economic alternative fuel for the future applications. They have similar properties to propane and butane, the principal constituent of LPG, and therefore can be used as a LPG substitute. Commercial catalysts used for the conversion of methanol and ethanol to suitable ethers are based on solid acid materials, such as γ-Al_2O_3 or zeolites, however due to side process of carbon deposit formation the catalysts with small pores (e.g. zeolites) can be quickly deactivated due to blocking of pore system by coke. The solution could be application PCH materials with pores larger than in zeolites, and therefore less susceptible for deactivation due to lower internal diffusion limitations.

PCHs obtained by intercalation of montmorillonite with SiO_2, SiO_2-Al_2O_3, SiO_2-TiO_2 and SiO_2-ZrO_2 pillars were characterized by high surface area, pore volume and relatively high surface acidity. Incorporation of titanium, aluminium or zirconium into the structure of silica pillars significantly increased their surface acidity and therefore also catalytically activity in the processes of DME and DEE synthesis. Catalytic performance of the PCH materials was correlated with the nature and strength of acid sites, which have been reported to play a key role in the studied catalytic processes. For the selected PCH based catalysts the long-term stability tests were done.

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Copper-based mesoporous silicas for SOx trapping applications: evolution of the adsorbent properties over cycling experiments

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Sulphur oxides (SO_x) represent a major air pollutant, coming from the combustion of fossil fuels in gas turbines for instance, that is controlled by national and international regulations. CuO/SiO_2 materials are known as SO_x trap materials. However, their large-scale development is still hampered by the sintering of the active phase over multiple adsorption and regeneration cycles, leading to the progressive decrease in SO_x adsorption capacities of the adsorbent. In this work, SBA-15 Organised Mesoporous Silica was functionalized with highly dispersed Cu^{2+}-based species (1). The as-obtained adsorbent was then assessed as a regenerable SO_x trap material. An extended characterisation, especially by XPS technique, was performed along with adsorption and regeneration cycles to correlate the evolution of the copper species and silica support with the performances of the adsorbent under different regenerative treatments. Thermal regeneration at 600°C under pure N_2 leads to the formation of Cu^+-based species (2), enabling a significant increase in SO_x chemisorption efficiency, which nevertheless decreases along cycles due to progressive sintering of the active phase, leading to bulky copper (II) oxide particles. Regeneration under reductive conditions (0.5 vol.% of H_2 in N_2) was then investigated as a way to decrease the regeneration temperature and limit this sintering process. It was found that the general behaviour of the copper-based species was very sensitive to the regeneration temperature. At 600°C, the active phase was completely converted into large metallic copper particles, giving rise to a fast decrease in SO_x adsorption capacity of the adsorbent due to partial obstruction of the SBA-15 silica porosity. Conversely, when this regeneration was performed at 280°C, the copper species remained as a highly dispersed phase on the silica support. That temperature is nevertheless too low to achieve the total decomposition of the sulphated active copper species in a reasonable time. It was eventually found that such a regenerative treatment can be isothermally performed with the adsorption step, allowing the material to do not suffer from any thermal shocks. Furthermore, the regeneration time does not exceed the sulphation time, allowing an easy industrial operation. In these conditions, the SO_2 adsorption capacities of the CuO/SBA material have been maintained over at least 25 cycles.

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Design and synthesis of stimuli responsive nanoporous silica supports for controlled drug delivery

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The growing interest for finding new, more efficient and reliable methods for treatment of human diseases and for more efficient drug administration, has induced a huge research devoted to the design and synthesis of new functional hybrid materials for controlled drug delivery. The design of site-specific and stimuli-responsive controlled drug delivery systems is of major interest for researchers worldwide [1]. Mesoporous silica nanoparticles (MSNs) appear as an appropriate materials because they are extremely effective solid supports which can be synthesized with an adjustable size, pore volume and pore diameter and which are suitable for drug storage and delivery due to their stability and no cytotoxicity [2].

In our work we have studied a functionalized nanoporous silica particles responsive to the change of pH or UV radiation. In the first approach we have investigated MSN of MCM and SBA type modified by the photosensitive derivatives of coumarin and p–coumaric acid, which are subject of reversible photodimerization under radiation and create a „gates“ on the surface [3]. The obtained results showed the possibility of controlling of the pore accessibility and/or drug release from MSNs by physical stimulus. In the second approach we studied pH-responsive platform consisting of cyclodextrin (CD)-capped MSNs. The pH-responsive nanovalves are composed of an amine-based stalk attached to the walls of silica nanoparticles that can bind β-cyclodextrin units non-covalently through supramolecular interactions. When the pH is decreased from its initial value (pH=7.4), the amine derivatives become protonated and the cyclodextrin caps were released and pores were un-blocked. In the third approach we have modified MSNs by the ligands (e.g. folic acid), which enable the vectored drug delivery to the tumor cells. The nonsteroidal antiinflammatory drugs naproxen and indomethacin as model drugs were employed in our works or we used an antineoplastic agent for the treatment of gastrointestinal cancers, 5-fluorouracil.

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Doping SBA-15 with Nickel Oxide by Freeze-Drying Impregnation

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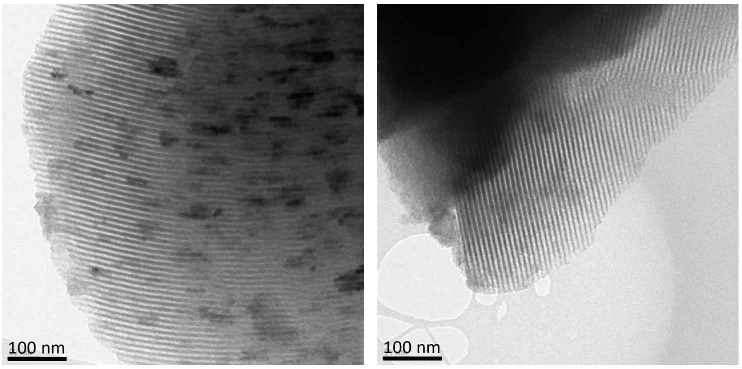
Immobilization of transition metal oxides on a solid support by impregnation with solutions of metal salts is a common route in catalyst design. An inherent difficulty of such methods is that precipitation by solvent evaporation leads to undesirably large catalyst crystallites forming at the outer surface of the porous support. In this study we explore the potential of an alternative route, based on eutectic crystallization of the aqueous metal salts in the pores of ordered mesoporous silica [1] and removal of ice by freeze-drying. The so-called two-solvents method was used to selectively load the pore space [2], i.e., to avoid an excess layer of salt solution coating the outside of the silica particles. The resulting samples were frozen with liquid nitrogen and lyophilized, then slowly heated to 500°C and calcined. A morphological and structural analysis of the formed nickel oxide species in the pores was performed and compared to samples prepared by conventional solvent evaporation.

The immobilized nickel oxide prepared by the new technique appeared in two morphologies: (a) crystallites of size somewhat smaller than the pore diameter of SBA-15 (7 nm); (b) material causing no XRD reflections but still detectable by energy-dispersive X-ray spectroscopy (EDX). Nitrogen sorption isotherms provided further information about the location of NiO in the pores: For samples containing NiO crystallites the pore size distribution (psd) of the primary pores was strongly broadened towards lower diameters. For samples showing no crystallites the psd remained narrow and was only weakly shifted, indicating that NiO was forming a layer at the pore wall.



TEM images SBA-15 doped with nickel oxide: sample with nickel oxide crystallites (left) and sample exhibiting slightly darker regions only (right).

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Synthesis and characterization of physisorption properties of novel core-shell systems with nanoporous organosilica shell and varying core materials

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Physisorption properties of pure nanoporous materials such as silica or metal organic frameworks (MOFs) are widely characterized. [1] In addition, different kinds of core-shell nanoparticles are well known, but often these core-shell nanoparticles consist of dense core materials (e.g. magnetite or gold). [2] Therefore, this work focusses on the synthesis and characterization of core-shell systems with a nanoporous core as well as a nanoporous shell with particle sizes in the nanometer range.

An example for such a new material are core-shell nanoparticles consisting of nanoporous silica nanoparticles (NPSNPs) as core and an organosilica shell due to a coating with periodic mesoporous organosilica (PMO) (Fig.1). [3] Just as the individual materials, the combination of NPSNP and PMO shows a high BET surface area as well as a large total pore volume, whereby the physisorption isotherms indicate the creation of cavities at the border between core and shell. Depending on the pore sizes of the core and shell materials, systems with bimodal pore size distributions can be received, which show up as individual peaks in the pore width distribution.

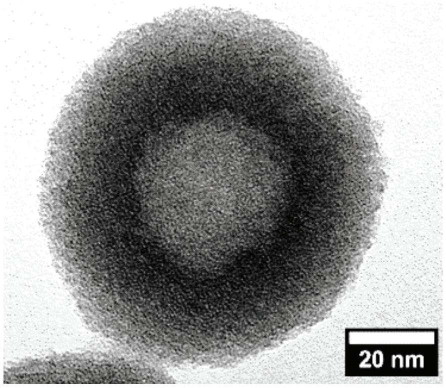

Figure 1: Core-shell nanoparticles of nanoporous silica and periodic mesoporous organosilica.

A conceivable application for such core-shell systems lies in drug delivery systems, exploiting the different chemical character of the particle parts for the dual release of different drugs. As another option, the porous organosilica shell can function as a diffusion barrier for sustained releases or as protection of a sensitive core material (e.g., MOFs).

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Nanoporous nanoparticles in drug delivery: Influence of release conditions on physisorption properties

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Nanoporous nanoparticles from silica nanoparticles or periodic mesoporous organosilica are promising materials for drug delivery applications due to their high permanent porosity, chemical variability and biocompatibility.[1] For this application, it must be taken into account that these materials degrade in aqueous media, a process which is further influenced by external parameters (e.g. release medium).[2] It is expected that porosity changes during release, but there are only few studies with regard to this aspect. Therefore, this work focusses on the synthesis and characterization of nanoporous silica nanoparticles (NPSNPs; Fig.1a),[3] nanoporous organosilica nanoparticles (NPOSNPs; Fig.1b) and core-shell-nanoparticles consisting of a NPSNP core and a NPOSNP shell (Fig. 1c)[4], and concentrates on the changes of their physisorption properties during a release study.

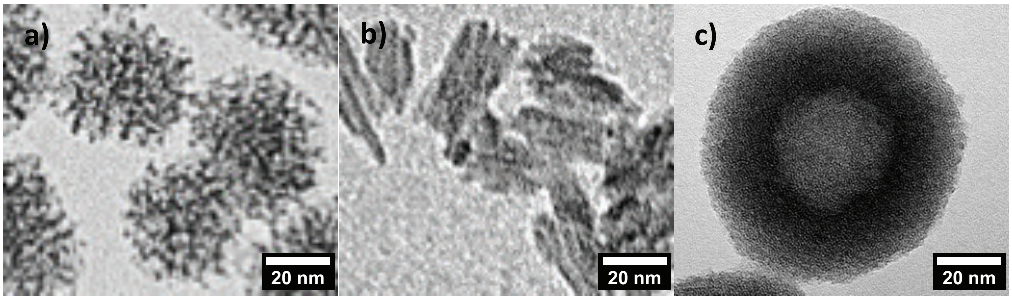

Figure 1: a) NPSNP; b) NPOSNP; c) core-shell nanoparticles.

For this study, these nanoparticles were loaded with the dye methylene blue, as reference nanoparticles were treated in the same way without the guest molecule. With these loaded particles, release experiments in phosphate buffered saline (PBS) were performed and after certain time intervals the release was stopped to characterize the influence of the release conditions on the particles on BET surface area, total pore volumes and pore size distributions at different times up to 10 weeks. Generally, a continuous decrease of the BET surface area and the total pore volume were observed, with a drastic drop at the beginning of the release.

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Template-Free Synthesis and Characterization of Mesoporous Organosilicas

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MCM-41 and PMOs are widely-studied classes of silica and hybrid organic-inorganic materials that can be prepared with surfactant templating (periodic mesoporous organosilica; PMO). A novel template-free method is presented for the synthesis of Mesoporous OrganoSilicas (MOS) (hybrid xerogels). The high surface area, high pore volume and tunable pore size of these materials make them attractive candidates as adsorbents, membranes and catalyst supports. We have used the cyclic organosilane precursor, 1,1,3,3,5,5-hexaethoxy-1,3,5-trisilacyclohexane (called 3R), in a template-free solgel polycondensation to produce a family of highly porous mesoporous organosilicas (MOS). These materials can be prepared with narrow pore size distributions, albeit lacking the ordered meso structuring provided by surfactant templating. By co-condensing 3R with other organosilane precursors a variety of compositions and functionalities can be incorporated into this high porosity platform. This talk will describe the synthesis and characterization of this family of 3R-MOS materials, and compare them to templated PMO analogues using the same precursor. The stability of the 3R precursor will be shown to be sensitive to the pH, temperature and time of gelation. Finally, methods for modifying the hydrophobicity of these materials and its impact on water adsorption properties will also be discussed.

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Reactivity of HD and its Simulants with Mesoporous Ceria Nanoparticles Functionalized with H_2O_2 Ligands

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ABSTRACT:

In this study, we synthesize mesoporous ceria nanoparticles with varying concentrations of H_2O_2 ligands for oxidative chemistry against mustard gas (HD) and its simulants. Ceria has been employed in a variety of applications for oxidative catalysis due to the ability of the cerium atom to coexist in two valent states ($Ce^{+3/+4}$), giving rise to a low activation barrier for the formation of an oxygen vacancy in the lattice. This vacancy has the ability to stabilize activated oxygen species, such as peroxides (O_2^{-2}) and radical species such as superoxides (O_2^-) that are regarded as being responsible for low temperature oxidation. The morphology and structure of the newly synthesized catalyst is characterized by N2 adsorption, SEM/EDS, XRD, TGA-MS and ATR-FTIR, while the reactivity is probed by the method of dose-extraction. Moreover, we demonstrate that the porosity can be tailored as a function of peroxide content, which positively correlates with its reactivity. Finally, results were corroborated with density functional theory (DFT) calculations to gauge the interaction of sulfur containing compounds such as H_2S with molecular oxygen at and nearby vacancy sites on the {111}, {110} and {100} facets.

Formation of Mesoporosity within Crystalline Metal-Oxide Nano-Crystals by Hydrogen Peroxide Treatment

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Metal-oxide nanoparticles (MONP) are widely used in several applications such as electrocatalysis[1], water purification[2], photo-catalysis[3], chemical warfare agent (CWA) decomposition[4], and others given that they are relatively easy to synthesize and cost-effective. Within the CWA decomposition field, MONP are particularly effective, as they have the ability to hydrolyze CWA and simulants, such as phosphor-organic and mustard agents into non-toxic products. Crystalline MONP nano-clusters typically exhibit low surface area. This means that their catalytic activity relies mostly on surface interactions. Surface chemistry within MONP nano-clusters play an important role into the adsorption and consequent decomposition of CWA. Therefore, incorporating mesoporosity within MONP can significantly increase the amount of active surface-sites, thus improving MONP overall catalytic activity. This work presents a facile-method for the formation of mesoporosity within crystalline MONP and investigates the mechanisms involved in the formation of such mesopores.

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Template-free Synthesis and Structural Evolution of Discrete Hydroxycancrinite Zeolite Nanorods from High-Concentration Hydrogels

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Abstract: We report a synthesis and characterization of hydroxycancrinite zeolite nanorods by a simple hydrothermal treatment of aluminosilicate hydrogels at high concentrations of precursors without a presence of structure-directing agents. Transmission electron microscopic (TEM) analysis reveals that cancrinite nanorods, with lengths of 200 – 800 nm and diameters of 30 – 50 nm, exhibit a hexagonal morphology and are elongated along the crystallographic *c* direction. The powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) and TEM studies revealed sequential events of hydrogel formation, formation of aggregated sodalite nuclei, conversion of sodalite to cancrinite and finally growth of cancrinite nanorods into discrete particles. The aqueous dispersion of the discrete nanorods displays a good stability between pH 6 – 12 with the zeta potential no greater than –30 mV. The synthesis is unique in that the initial aggregated nanocrystals do not grow into microsized particles (aggregative growth) but into discrete nanorods. Our findings demonstrate an unconventional possibility that discrete zeolite nanocrystals could be produced from a concentrated hydrogel.

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NSF Travel Grant; National Institute of Allergy & Infectious Diseases; NSF Small Business Innovation Research (SBIR) Phase I & II; LeRoy Eyring Center for Solid State Science; Remylop, LLC; Gatan, Inc for the loan of K2 IS camera.

CPM8 | POSTER PRESENTATION
ADVANCED MATERIALS: CARBONS

Adsorption of Acetaminophen on Activated Carbons from Cashew Nut Shells

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Activated carbons were prepared from cashew nut shells by chemical activation of shells with phosphoric acid and heat treatment at elevated temperatures. Prepared activated carbons were studied for the adsorption of acetaminophen. Acetaminophen and other pharmaceuticals are found in ~ 80% of wastewaters in the U.S. Acetaminophen is considered to be the most common cause of acute hepatic failure and the second most common cause of liver failure in humans.

The effect of phosphoric acid impregnation ratio and heat treatment temperature on the adsorption of acetaminophen were studied. Equilibrium adsorption data had the best fit to Langmuir model for all the carbons. It was found that the impregnation ratio has little effect on the adsorption of acetaminophen, which is likely related to the insignificant differences in porosity and the amount and nature of surface functional groups present on the surface of the carbons as a result of impregnation. Carbons impregnated at higher ratios had slightly lower adsorption capacities due to a high amount of surface groups possibly blocking the pore entrances. These groups are expected to be mostly oxygen- and phosphorous-containing. The nature of surface functional groups will be studied using Fourier transform infrared spectroscopy (FT-IR) and X-Ray photoelectron spectroscopy. The heat treatment of the shells in the temperature range 400-700 °C showed the increase in the aromatization of carbons upon increase in temperature, which is related to the removal of surface functional groups and increase in porosity. The latter one will be studied using nitrogen sorption.

The adsorption capacity of acetaminophen increased from 400 to 600 °C, peaking at 600 °C and going down at 700 °C. Carbon prepared at impregnation ratio of 1.7:1 (H_3PO_4:shells) and heat treated at 600 °C showed the highest adsorption capacity for acetaminophen (160 mg/g). It is possible that the right combination of porosity and surface chemistry of this carbon resulted in its best performance for acetaminophen adsorption.

Acetaminophen and salicylic acid adsorption on chemically modified activated carbons: Effect of the ionic strength on the adsorption thermodynamic functions.

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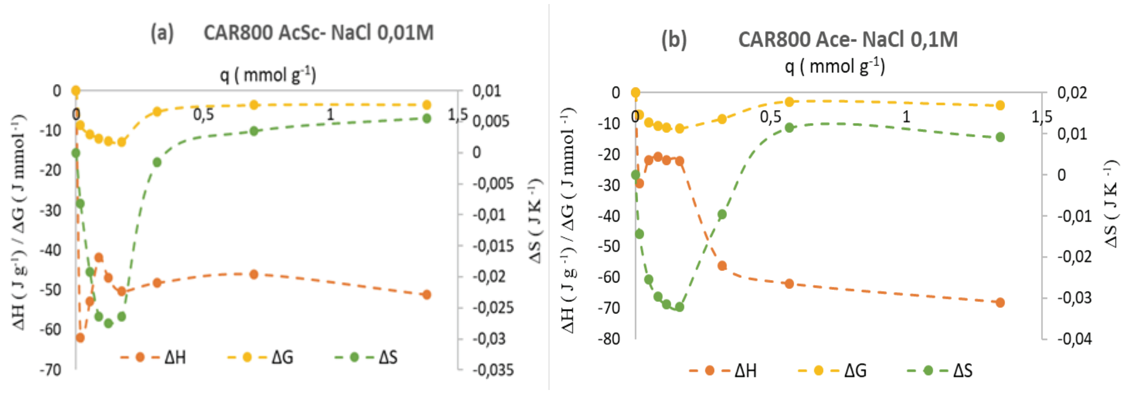
The use of activated carbon as adsorbent has been evaluated as an effective alternative for the removal of pharmaceutical molecules in clinical and environmental scopes [1].

In this work, we evaluated the effect of the ionic strength on the acetaminophen and salicylic acid adsorption in two samples of granular activated carbon, CAG corresponds to a commercial activated carbon CARBOCHEM GS 75© prepared from coconut shell and physical activation with CO_2; the sample of activated carbon, CAR 800, was obtained by heating the sample CAG heat treatment for 2 hours at 800 °C. The adsorption tests were carried out with concentrations of acetaminophen and salicylic acid between 0.06 mmol L^{-1} and 7.2 mmol L^{-1}, the ionic strength was adjusted with solutions of NaCl 0.01M and 0.1M.

The results indicate that the adsorption process is favored for both compounds in the reduced activated carbon, CAR 800, this may be related to the increase of π electrons in the graphenic layers that can interact with the adsorbates, which are weak acids [2].

It was determined that the adsorption of salicylic acid is favored at low values of ionic strength, contrary to acetaminophen whose adsorption capacity increases with ionic strength. Figure 1 shows the thermodynamic functions change (ΔG ΔH and ΔS) for the adsorption process on activated carbon CAR 800 (a) salicylic acid in solution of NaCl 0.01M (b) acetaminophen in 0.1M NaCl solution.



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Photocatalysis with Activated carbon prepared by phosphoric acid activation of Palm Kernel Shell: Porosity effect

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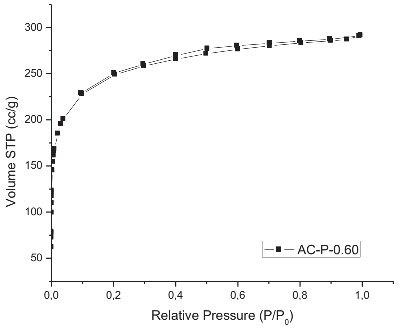
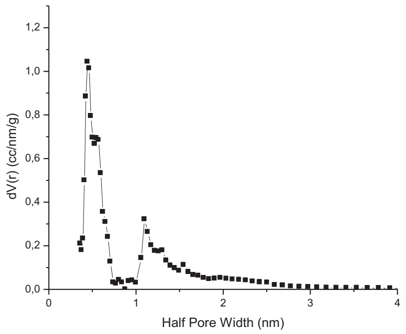
TiO_2 has been reported as a more effective photocatalyst [1]. However, the particle size of TiO_2 has been estimated to be in the order of 5 to 60 nm, which makes it more difficult to separate TiO_2 from a solution, especially in large-scale systems. For this reason, this work involves finding solutions to prepare photocatalysts with a larger particle size that allow the combination of textural, structural and chemical properties to achieve better efficiency in these processes.

The advantage of using AC is to obtain a high surface area where the particles can be distributed and immobilized [2]. The textural parameters obtained with phosphoric acid as activating agent is 919 m^2/g, DA: n=1,20; Vmicro, DA=0,425 cc/g; Radio Poro=0,77 nm; E = 5,378 kJ/mol. The PSD show a Activated Carbon Heterogeneous with Slit/Cylindr Pore, QSDFT (% Error = 0,077).





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Adsorption and immersion enthalpy study of benzene, cyclohexane and hexane on modified activated carbons.

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Adsorption isotherms of benzene, cyclohexane and hexane are determined from the gas phase on microporous granular modified activated carbon. The Dubinin-Radushkevich equation was used to calculate the parameters of characteristic energy E_o and micropore volume W_o. Also, immersion enthalpies of activated carbons in solvents were obtained, and they were used to calculate the product E_oW_o with the Stoeckli and Kraehenbuehl equation. Subsequently, a correlation between E_oW_o by the two techniques was obtained and a relationship with some adsorbate characteristics such as molecular size, the molar volume and dielectric constant was established. It was found that the solid modifications affect the adsorption process, being favoured by temperature changes and restricted by oxidation processes performed for chemical modification. The adsorbate which showed the highest values for the E_oW_o product was benzene, due to it being the solvent with a smaller molecular size, lower molar volume and higher dielectric constant.

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Pore Size Effects on Partial Breaking of Coulombic Ordering Structure of Ionic Liquids in Carbon Nanopores

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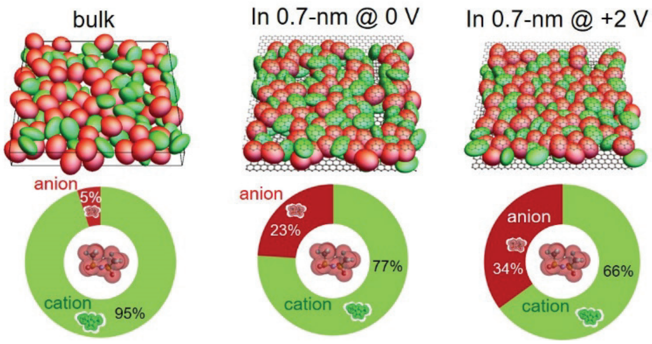

Fig. (top) Ionic liquid structure with HRMC simulation. (bottom) The population of ions around a central anion.

Nanoporous carbon materials have great advantages for application to the electrodes of electrical devices like suppercapacitors because of their high surface area and high electrical conductivity, being unique compared with zeolites and MOFs [1]. However, the understanding of the ionic systems in carbon nanopores, which is directly related to understanding of mechanism of supercapacitors, is still limited due to the difficulty for elucidation of the nanoscale structure in the confined nanopores with experiments. In 2011, Kondrat and Kornyshev theoretically showed the unique structure formation of "superionic state" in which ions of same charges confined in one molecular size of nanopores by conductive pore walls can be closer each other, because of the effective electrostatic screening effect from the conductive pore walls [2]. Recently, our group succeeded to evidence the partial breaking of Coulombic ordering structure of ionic liquid in sub-nanometer carbon pores with Hybrid reverse Monte Carlo (HRMC) simulation-aided X-ray scattering technique [3]. The population of anions around a central anion is 23 % in 0.7 nm carbon nanopore, indicating almost 5 times larger than that of bulk ionic liquid. Furthermore, this non-Coulombic ordering intensively varies on application of an external electric potential. In our presentation, we will show the detailed pore size dependences of ionic liquid structure in carbon nanopores with our HRMC method.

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Preparation of low-cost activated carbons from bio-waste for quantum sieving applications

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Huge production of waste agriculture materials causes environmental concerns, so using and recycling of such kind of waste materials to high-tech applications are extremely appreciated. Globally, the amount of waste is about 1.3 billion tons and continues to increase, and bio-waste accounts for a large part of it. In this study, peanut shell, ginkgo leaf and metasequia leaf as waste agriculture products were recycled by carbonization converting them to nanoporous carbonaceous materials. Nitrogen adsorption–desorption isotherms confirmed the highest specific surface area(SSA) and narrow pore size of low-cost activated carbons, exhibiting ca. 800 m^2/g SSA with ca. 4.0 Å of the average half-pore width. Recently, the separation of hydrogen isotopes mixtures is one of the challenges in modern separation science and technology due to its almost identical size, shape and thermodynamic properties of each other. As quantum sieving in confined space has received increased attention as an efficient method for hydrogen isotope separation, this small and narrow pore size distribution of our low-cost activated carbons can be exploited as a quantum sieving material for hydrogen isotope separation. Hence we experimentally investigate D_2/H_2 molar ratio at various temperature of 20 K ~ 77 K and calculated the selectivity through IAST (ideal adsorption solution theory) method. Obtained results are also compared with commercial activated carbon (Norit GAC 1240).

Heteroatoms-decorated hierarchical porous carbons derived from biomass for propane dehydrogenation

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Key words: nanocarbons; propane dehydrogenation; propylene; metal-free catalyst

Nanocarbon materials, such as nanodiamond, carbon nanotubes (CNTs) and ordered mesoporous carbons (OMCs), are regarded as promising metal-free catalysts in heterogeneous catalysis due to their large surface area, rich pore structure and tunable functional groups [1-3]. From an environmental point of view, nanocarbon catalysts enable a clean disposal by combustion after a certain life-time, making them attractive alternatives to noble metal or metal oxide catalysts for a more sustainable catalytic reaction. Our recent work demonstrated that ordered mesoporous carbons (OMCs) were robust catalysts in direct dehydrogenation (DDH) of propane, due to their large porosity and numerous oxygenated functional groups [4-7]. However, the production of nanodiamond, CNTs, OMCs, especially the corresponding heteroatoms-doped nanocarbons, is so complex, time-consuming and much expensive, which is unfavorable for commercial application. So, the exploitation of a new nanocarbon with both rich porous structures and heteroatoms by a simple and cost-effective way for dehydrogenation reaction is very urgent and important.

Herein, we provide examples for preparation of heteroatoms-decorated porous carbons through alkali and/or acid treatment of biomass wastes (such as chestnut shells, bean dregs and shaddock peel). The activation parameters including activator types, dosage, temperatures are all compared in detail. And the amounts of functional groups along with the porous structures would be significantly affected by the activator/C ratios and calcination temperatures. Fig. 1 shows an example of shaddock peel derived nanocarbons before and after activation by H_3PO_4 at 600 ^{o}C, showing that both the micro-/meso-/macropores and heteroatoms are introduced into the biomass-derived nancarbons after activation. The activated carbon materials were used as catalyst for propane dehydrogenation, exhibiting improved catalytic performance. And the surface functional groups combined with the hierarchical porous structures are responsible to the high catalytic performance.

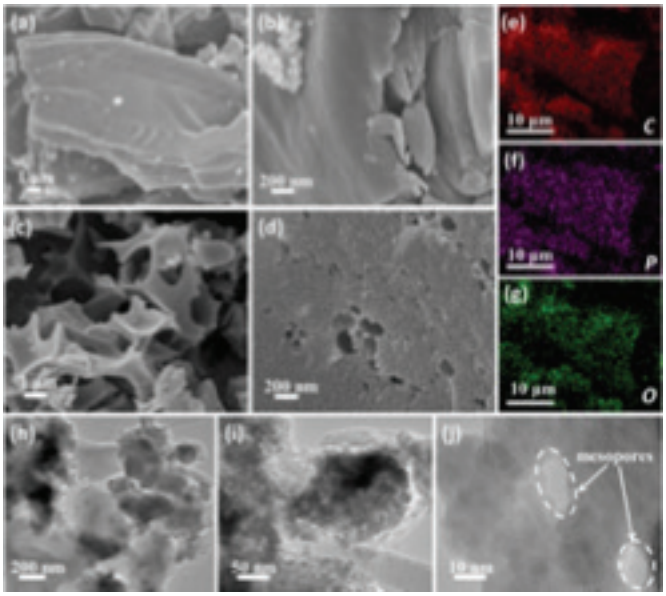

Fig. 1 SEM and EDS element mapping images of shaddock peel derived nanocarbons before (a, b) and after (c-g) activation by H_3PO_4 at 600 °C. (h-j) TEM images of shaddock peel derived nanocarbons after activation by H_3PO_4 at 600 °C.

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Boron-doped microporous activated carbon with enlarged surface area for efficient oxygen reduction and CO_2 capture

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Key Words: Activated carbon; Boron; Doping; Oxygen reduction; CO_2 capture

Featuring advanced properties, including low-cost, abundance, and easy-preparation, metal-free carbonaceous materials exhibit huge potential in tremendous applications, such as Li-ion battery, electrocatalysis, supercapacitors, photocatalysis, biomass conversion and adsorption. Furthermore, the abundant porosity of carbons has positive effect on reaction process, due to enhanced mass transport and more exposed active sites. Thus, the porous carbon with larger surface area exhibits improved performance on energy conversion/storage and adsorption. Moreover, heteroatoms-doping and activation are all effective approaches to modify the chemical and physical properties of carbonaceous materials. Up to now, through various types carbonaceous materials have been synthesized, rarely attention has been focused on the commercial activated carbon which has low-cost, high specific surface and abundant microporous network.

Therein, taking advantages of the larger specific surface area of commercial activated carbon, we demonstrate our attempt to prepare B doped microporous activated carbon with enlarged specific area in the presence of potassium tetraborate under pyrolysis activation, wherein the potassium tetraborate works as activating agent and B source. The synthesis of the B-doped activated carbon is carried out through two steps consisting of the mixture of potassium tetraborate and commercial activated carbon, and high-temperature pyrolysis activation. Finally, the microporous carbon with surface area as high as 1424 m^2 g^{-1} and 4.34 at% B is obtained. The resultant material with optimized textual properties and more exposure active sites ensures outstanding activity and durability for electrocatalytic oxygen reduction, additionally, exhibits excellent capture capacity for CO_2 uptake as absorbents. The synthetic method reported in this study towards microporous activated carbon with heteroatoms dopants provides the effective route to fabricate metal-free multifunctional alternative for energy or adsorption applications.

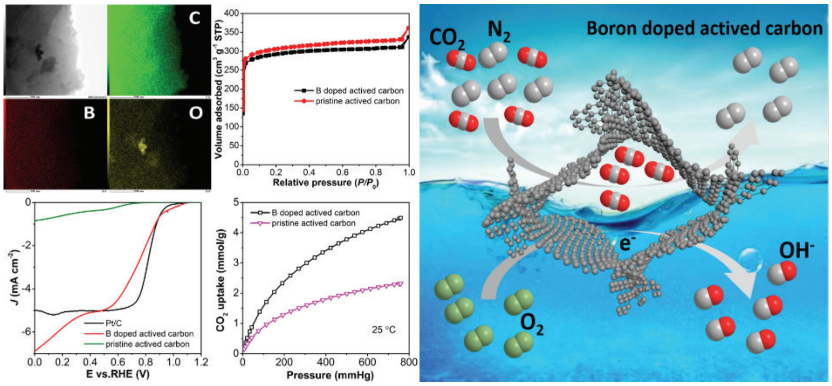

Figure 1 The preparation of boron doped active carbon for oxygen reduction and CO_2 capture.

Surface and interface engineering of heteroatoms-doped porous carbon materials for efficient electrocatalytic processes

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Key Words: Carbonaceous materials; Heteroatom-doping; Porosity; Electrocatalysis

Carbonaceous materials have become one of the hotspots of interdisciplinary research because of its unique physical and chemical properties and structure. It has shown great potential in the fields of electrocatalytic oxygen reduction, oxygen evolution and hydrogen evolution. However, the electrocatalytic performance of modified carbonaceous materials still fall short of replacing the state-of-the-art noble metal materials, mainly due to the insufficient electrochemically active centers. The chemical and physical flexible of carbonaceous materials give them great potential to further improve the electroactivity even further. The introduction of fine pore structure and high specific surface area into the architecture of the carbonaceous material by different methods contributes to the improvement of mass transfer and the exposure of the active sites, thereby improving the electrocatalytic performance. At present, commonly used research methods include heteroatom doping, enlarged specific surface area and introduction of transition metal components to achieve impressive catalytic activity to replace the noble electrocatalysts. Breaking bottlenecks of the traditional preparation of the catalyst, looking for other efficient preparation methods and to ensure the electrocatalyst activity and stability is imminent.

With a thoughtful understanding of structure – activity relationship, a series of heteroatoms-doped carbonaceous material with well-defined porosity were prepared. Taking consider of the cross-linking effect between base melamine and organophosphonic acid on the basis of acid − base conjunction to initiate the preparation of polymer analogues, nitrogen and phosphorus co-doped carbonaceous framework supported metal phosphide[1] and heteroatom-doped porous carbons[2] were prepared and exhibited impressive hydrogen evolution and oxygen reduction performance, respectively. Using the organophosphonic acid salts as the porogen and phosphorus source, phosphorus-doped mesoporous carbon,[3] and nitrogen and phosphorus dual-doped microporous carbon spheres[4] were obtained and both of them exhibited high oxygen reduction activity. Under the guidance of surfactant-induced self-assembly, the nitrogen and sulfur co-doped hierarchically porous carbons[5] and nitrogen and sulfur co-doped mesoporous hollow carbon microspheres[6] were prepared and employed as highly efficient oxygen reduction electrocatalysts. In summary, we hope our works can provide new insight into the designing of carbon-based catalysts, particularly understanding the electrochemical performance and reaction mechanisms from the view of chemical composition and structural properties.

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Modified red mud with hierarchical meso-/macroporous structure for efficient oxidative desulfurization reaction

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Key words: modified red mud; modification; oxidative desulfurization; meso/macropores

Sulfur compounds are undesirable in fuel oil, which are toxic to some catalysts in refining process and resulting in sulfur oxides (SO_x) in combustion [1]. Oxidative desulfurization route has been regarded as a very efficient way for desulfurization. Up to mow, many kinds of catalysts such as ionic liquids, VO_x and MoO_x have been demonstrated efficient catalysts for desulfurization [2]. However, the strong toxicity of V and hard separation system of ionic liquids limit their wide application. And the exploitation of new environmental-friendly catalysts with both low cost and high activity is very important and necessary. Recently, preparation of industrial catalysts based on waste materials has drawn wide attentions. Red mud (RM), an aluminum industry waste, cause serious environmental problems due to its high alkalinity and large heavy metal contents. And the disposal and re-use of RM is of great interest all over the world. Our recent works have showed that RM after treated by acid and alkali possess large surface area and porous structure, which can be used as good supports for various reactions including ammonia decomposition [3, 4], waste water treatment [5], and CO oxidation [6, 7]. Herein, different solvent and acid (H_2O, HCl, HSO_4 and H_3PO_4) were used to modify RM. After modification, the porous structure and surface area of the acid-treated RM increased sharply (Fig. 1 and Fig. 2). And the modified RM was directly used as catalysts for oxidative desulfurization dibenzothiophenes, which exhibited high catalytic activity. After 10 min, almost no dibenzothiophenes can be detected, suggesting a very promising catalyst if desulfurization (Fig. 3). Importantly, this catalyst comes from industry waste, has much low cost, and represents a new rout for the utilization of red mud.

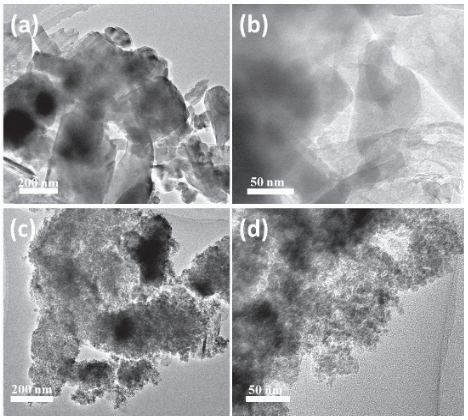

Fig. 1 TEM images of the raw RM (a, b) and HCl-modified ARM.

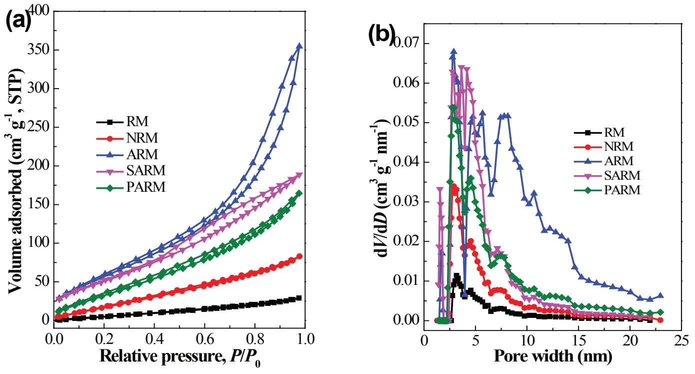

Fig. 2 N_2 adsorption-desorption isotherms (a) and the corresponding pore size distribution (b) of raw RM, natural RM (NRM) and different acid-treated RM.

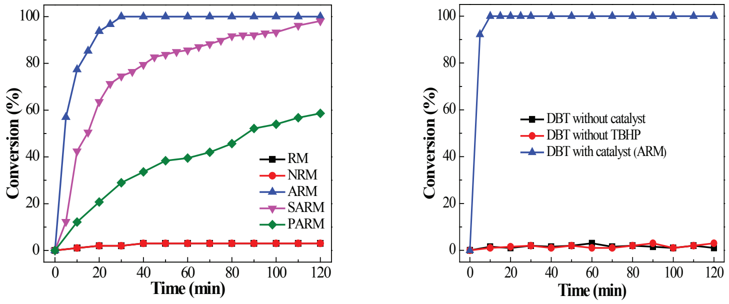

Fig. 3 (a) DBT conversion over the RM and modified RM, (b) DBT conversion with/without ARM catalysts (reaction condition: 10 g MD 500, 0.05 g ARM, O/S = 3:1).

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Nanocarbons as metal-free catalysts for propane dehydrogenation reaction

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Key words: nanocarbons; propane dehydrogenation; propylene; metal-free catalyst

Catalytic dehydrogenation of propane to propylene has drawn increasing attention worldwide due to the growing demand of propylene in petrochemical industry. Over the last several decades, Pt- and Cr-based catalysts were demonstrated efficient catalysts in propane dehydrogenation [1]. However, the high cost of Pt and strong toxicity of Cr limit their wide application. And the exploitation of an alternative catalyst with high activity and much low cost is urgent and necessary. Recently, nanocarbons as metal-free catalysts were found to be good catalysts in dehydrogenation reactions, which were regarded as promising alternatives for the noble metal or transition metal oxide catalysts [2]. Our recent work also demonstrated that ordered mesoporous carbons (OMCs) were robust catalysts in direct dehydrogenation (DDH) of propane, duo to their rich porous structure and numerous oxygenated functional groups [3-6]. However, the catalytic activities of these nanocarbons catalysts are really low, which need to be further improved.

Herein, we provide examples of the modification of carbon materials through alkali and/or acid treatment. The applications of modified carbon materials for propane dehydrogenation are tested and discussed in detail. The modified parameters including activated precursor, methods, temperature are all compared in detail. After modification, several properties such as morphology, surface functional groups, and porous structure of nanocarbons would be greatly changed. And the surface oxygenated functional groups combined with the hierarchical porous structures are responsible to the high catalytic performance.

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Curious Behavior of Polymer of Intrinsic Microporosity / Activated Carbon Composites for Hydrogen Storage Applications

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Polymers of Intrinsic Microporosity (PIMs) have attracted the attention of researchers in the last decade due to their high gas adsorption capability, which results from the combination of high surface area and favorable pore size distribution [1]. These materials owe their extraordinary properties to a rigid polymer backbone that prevents efficient space packing by polymer chains thus creating microporous voids (*i. e.*, pores narrower than 2 nm), which can be used as compartments to store gas molecules with enhanced density. This is of particular interest for hydrogen storage applications where volumetric energy density is of key significance. Here we focus on PIM-1, which is soluble in organic solvents. It offers the capability of forming films which could be applied as liners for hydrogen storage tanks, thereby enhancing hydrogen capacity or reducing operating pressure. We have investigated PIM-1 as a medium for hydrogen storage and demonstrated enhanced surface area using powdered fillers [2].

In this study we are exploring a composite of PIM-1 and an activated carbon (AX-21) with very high surface area (3 000 m^2g^{-1}) and a relatively low density. This enables membranes with a high filler content to be obtained without loss in mechanical properties. Adsorptive characterization has shown significant improvement in hydrogen uptake. Mechanical properties were observed to be uncompromised, even at high concentrations of carbon filler in PIM-1 (50 wt%).

In addition to their potential for storage application, an intriguing curling phenomenon of composite films was observed which might be of interest for sensing or actuation. Films formed by means of casting curl up into a roll during evaporation, and this behavior is reversed by moistening the film with ethanol. Curling would repeat upon ethanol evaporation. The direction of curling can be controlled by clamping the film and was observed to be completely reversible and repeatable. The loads produced by curling were able to lift objects several times heavier than the film itself. Detailed mechanical and structural analysis was performed to further explore and understand this phenomenon. This opens new potential field of applications such as actuating adsorptive matrices which can be used in active storage systems for gas or controlled release media.

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CPM8 | POSTER PRESENTATION

ADVANCED MATERIALS: OTHER

Design and characterization of layered solid from the intercalation of organic molecules into transition metal nitroprussides.

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The design and development of hybrid materials obtained from the assembly of organic and inorganic units constitutes one of the most fertile and emerging areas within the science of materials. The wide variety of building blocks that exist has allowed the construction of a large variety of 1D, 2D and 3D[1] structures that have received great attention for their attractive properties that have found a wide variety of applications in fields such as catalysis, energy storage, the development of electronic devices, biomedicine, environmental remediation, among others[2,3].

Laminar materials are the result of preferential growth in two dimensions related to the electronic structure of the atoms involved. These materials can also be obtained from 3D lattices, in which growth in the axial direction is inhibited[4]. Particularly the pentacyanonitrosilferrate $[Fe(CN)_5NO]^{2-}$ anion commonly known as nitroprusside ion, can act as a bridge unit between coordinating metal centers to give rise to a series of coordination compounds which is usually obtained as 3D solids, except phase of Cu(II) which is obtained in laminar form[5].

In this contribution, we used the different organic molecules as 1-methyl-2-Pyrrolidone (1m2p), Pyridine (Py) and 4,4-Bypiridine (Bipy) to inhibit the axial growth of the transition metal nitroprussiate phases for the remaining metals (M = Mn, Fe, Co, Ni, Zn). The obtained materials were separated by centrifugation, washed and then characterized by chemical analyses, XRD, IR, UV−vis, TG, magnetic data and absorption gases techniques.

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Unusually strong dipole-dipole and dipole-quadrupole interactions in $(VO)_3[M(CN)_6]_2 \cdot nH_2O$ with M = Fe, Co

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In porous Prussian blue (PB) analogues, the partially naked metal centers at the cavities surface are responsible for many of their physical properties [1-7], among them the adsorption potentials [8-9]. In the as-synthesized PB analogues, such metal sites stabilize water molecules inside the cavity through coordination bond formation. The filling of the cavity volume is completed with water molecules linked to the coordinated ones through hydrogen bonds formation. Vanadyl-based PB analogue shows quite different features. The metal (V) at the cavities surface has saturated its coordination sphere with the O atom of the vanadyl ion (V=O). In this material, the V=O group preserves enough strong dipole moment to stabilize adsorbed species in the cavity through dipole – dipole and dipole-quadrupole interactions. This contribution reports the preparation, crystal structure and properties for $(VO)_3[M(CN)_6]_2 \cdot nH_2O$ with M = Fe, Co. According to the refined crystal structure, IR spectra and TG data, six water molecules remain stabilized inside the cavities through a strong dipole-dipole coupling with the vanadyl group. The cavity contains additional water molecules interacting through hydrogen bond bridges with the water molecules coupled with the V=O group. The vanadyl ion is free of hydrogen bonding interactions with the water molecules. The recorded adsorption isotherms for N_2, CO_2 and H_2, three molecules with only quadrupole moment, reveal presence of relative strong adsorption forces due to dipolequadrupole interactions.

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Various Cationic ((Sr^{2+}, K^{+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, and Li^{+})) Exchanged Clinoptilolite As a Adsorbent for CH_4/N_2 Separation

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CH_4/N_2 separation by adsorption is based on the unique adsorption property of microporous materials with high selectivity, which allows N_2 molecules (kinetic diameter 3.6 Å) to diffuse quickly while hindering the diffusion of slightly larger CH_4 molecules (kinetic diameter 3.8 Å). Recently, a wide variety of porous materials, such as zeolite 4A, zeolite 13X, and carbon molecular sieve have been used for CH_4/N_2 separation via pressure swing adsorption (PSA) technology, particularly the clinoptilolite containing various metal cations [1]. These cations are mutilvalent and hence they form strong electrostatic interactions with CH_4 molecules (as well as N_2). Therefore selection or development of appropriate the cationic exchanged clinoptilolite as a absorbent for PSA industry has been attracting the attentions in the applications of energy and environmental fields.

Herein, we focused on the various cation (Sr^{2+}, K^{+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, and Li^{+}) exchanged clinoptilolites, and the aim of this work is to investigate their thermodynamic properties and diffusion behaviors in order to potentially enhance selectivity of CH_4/N_2. The Na, K-clinoptilolite was firstly synthesized according our previous report, and then ion-exchanged using mixture of 1g solid and 100 mL aqueous solution with 1.0 M chlorizated salts at 80 °C and stirred for 2 hours. After that, the solution was decanted and a 100 mL fresh solution of chlorizated salts was added, this ion-exchange procedure was repeated 3 times. Finally, the samples were vacuum filtered after the final ion-exchange, washed with copious amounts of deionized water, and air dried at 150 °C for 6 hrs. Figure 1 shows the XRD patterns of resultant various cation exchanged clinoptilolites, which presented the typical diffraction peaks of clinoptilolite, suggesting the heulandite structures could be remained after ion-exchange and therefore no significant effect on the microscopic ordering during ion exchange treament. These observations could be further confirmed by SEM micrograph (unshown), showing a sharp and complete plate-like morphologies in size of around 10 μm. Meanwhile, Their structural properties and textural parameters of before and after ion exchanged are under way by various characterizations, such as XRD, TEM, BET, FT-IR, TG, ^{29}Si MAS-NMR.

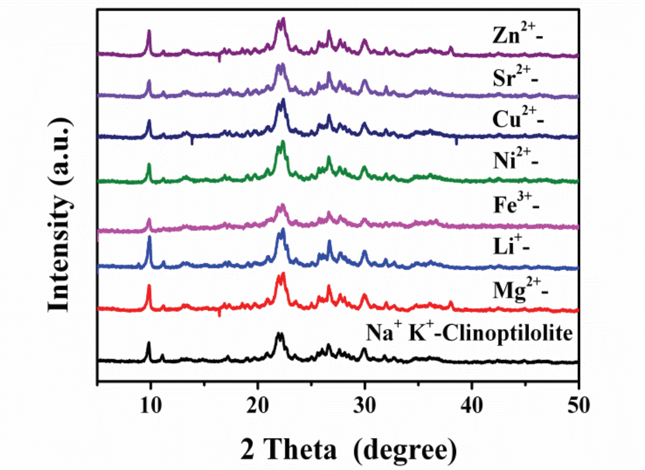

Figure 1. XRD patterns of ion-exchanged clinoptilolites

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Simple and competitive adsorption study of Nickel (II) and Chromium (III) on the surface of the brown algae *D. antarctica biomass*.

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The pollution produced by heavy metals in the environment has become a major problem worldwide, because of their high toxicity and bioaccumulation [1]. The maximum allowable industrial discharge limit of Ni^{2+}, Cr^{3+} and Cr^{6+} ions is 3.0, 1.0 and 0.1 mg L^{-1}, respectively. In this work, the biomass obtained from the algae *D. antarctica* was used to bioadsorb these metal ions and separate them from the aqueous medium. The procedure used is described below:

Initially the biomass was prepared and characterized by SEM, IR spectroscopy, physisorption of N_2, immersion calorimetry, thermogramometric analysis and Boehm titration. The optimum pH and time values were determined for the adsorption of Ni^{2+} and Cr^{3+} metal ions, it was found that the optimum pH for this biosorption process is 5 for both contaminants and that the time required to reach the equilibrium is 240 and 420 min for Ni^{2+} and Cr^{3+} respectively; subsequently, the biosorption experiments of the metal ions were carried out. In these experiments it was found that the value of Q_o for Ni^{2+} and Cr^{3+} is 32.85 and 102.7 mg g^{-1}, respectively. The data obtained in the bioadsorption experiments were fitted to the Freundlich, Langmuir, Redlich-Peterson, Sips and Toth models, in order to describe the adsorption phenomena on the surface of the bioadsorbent. It was found that for both contaminants, the Sips model presented the best fit to the data obtained, indicating that adsorption of Ni^{2+} and Cr^{3+} ions assumes that each adsorption site interacts with a single molecule of adsorbate. It should also be mentioned that this is a three-parameter model and the adsorption sites on the surface of the biomass are distributed homogeneously and heterogeneously. This was corroborated by SEM micrographs.

In addition, competitive adsorption experiments were performed between Ni^{2+}-Cr^{3+} and Ni^{2+}-Cr^{6+} ions. In all the tests performed the concentration of the Cr^{3+} and Cr^{6+} ions were of a constant value of 100 ppm; while the Ni^{2+} ion concentration was 7.5, 25, 50, 100, 150, 200 and 300 ppm. In general, it was found that in the competitive bioadsorption between Ni^{2+} and Cr^{3+} is favored by the initial concentration of the metal ions; while in the competition between Ni^{2+} and Cr^{6+} it was determined that the affinity of the surface of the biomass is greater towards the Ni^{2+} ion regardless of the value of its initial concentration.

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Characterization of converter sludge as sorbent and utilization for mine water cleaning

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Awareness of environmental impacts and concern for the environment has been increased in recent decades. Water management strategies of the international mining industry are used to minimize the environmental impact of mining operations, and these are now at the heart of mine development. In order to protect of environment, the quality of water leaving mine sites is not adversely affecting water users downstream, mining companies develop water management plans to minimize the potential of water contamination, and to prevent the release of polluted water into the environment. There is a number of different treatment technologies available to clean contaminated water. Depending on the desired final water quality, a mine may also use other technologies, namely ion exchangers, membrane filters, and reverse osmosis. These purification methods are very expensive and need a many chemicals and also human support. Utilization of low-cost sorbent from waste product is a good possibility and an alternative to existing methods [1].

The aim of this paper was to characterize the properties of waste from metallurgical industry from process of gas treatment in an oxygen converter. This paper studies of utilization of converter sludge, its sorption properties and the possible way to use this waste material as sorbent. The main idea of this research is use this waste as sorbent for mine water treatment plant. Sorbent was utilized for a reduction of content of problem metal ions in mine water. The secondary idea was reduction of costs necessary for the cleaning mine water before drain to the watercourse [2].

Converter sludge was characterized by X-Ray diffraction, SEM, XRFS spectroscopy, specific surface area and particle size. Sorption experiments were conducted in batch mode by using distilled water and real mine water. Removal efficiency dependencies on pH, contact time, initial concentration were establish. The sorption kinetics was evaluated with pseudo-first and pseudo-second order kinetic model. The optimal conditions obtained from experiments of distilled water after that were applied to determine the efficiency of removal from the mine water. For tested materials, the highest level of mine water purification was achieved and mine water can be discharged into the watercourse. The results of this study indicate that the metallurgical waste as sorbent is highly effective for the treatment of multicomponent mine water.

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Development of Structured Porous Adsorbents Using 3D Printing Technique for CO_2 Capture

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Abstract

Porous adsorbents such as zeolites, amine based sorbents and metal-organic frameworks (MOFs) in their traditional configurations failed to provide superior CO_2 adsorption strategies when implemented to large scale application. In this study, zeolite, aminosilica and MOF monoliths with novel structures were fabricated using three dimensional (3D) printing technique and their CO_2 adsorption performance was investigated.[1]–[3] The physical and structural properties of 3D printed monoliths were evaluated and compared with their powder counterparts. To enhance the adsorption performance, 3D printed zeolite and MOF monoliths were developed with varied and optimized weight fractions of binder, co-binder and plasticizer whereas 3D printed aminosilica monoliths were formulated using pre-synthesized silica incorporated with tetraethylenepentamine (TEPA) and poly(ethylenimine) (PEI) adsorbents using three different approaches. In addition of TEPA and PEI, 3D printed silica monoliths were prepared and post-functionalized with 3-aminopropyltrimethoxysilane (APS). Our results indicated that 3D-printed monoliths with high adsorbent loadings exhibit adsorption uptake that is comparable to their corresponding powders. In addition, the printed zeolite and MOF monoliths showed reasonably good mechanical stability that can eventually prevent attrition and dusting issues commonly encountered in traditional pellets and beads packing systems. 3D printed monolithic adsorbents exhibited relatively fast dynamics than their powder analogue at 25 ºC and 1 bar. The 3D printing technique offers an alternative, cost-effective, and facile approach to fabricate structured adsorbents with tunable structural, chemical, and mechanical properties for use in gas separation processes.

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CPM8 | POSTER PRESENTATION

ADVANCED MATERIALS: MOFS

Enhancing Van der Waals interactions of functionalized UiO-66 with oxygen and other non-polar gases via electron donation to the metal-organic framework linker

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UiO-66 is a highly stable metal-organic framework (MOF) that has garnered interest for many adsorption applications. For small, nonpolar adsorbates, physisorption is dominated by weak Van der Waals interactions limiting the adsorption capacity. A common strategy to enhance the adsorption properties of isoreticular MOFs, such as UiO-66, is to add functional groups to the organic linker. Low and high pressure O_2 isotherms were measured on UiO-66 MOFs functionalized with electron donating and withdrawing groups. It was found that the electron donating effects of $-NH_2$, -OH, and $–OCF_3$ groups enhance the uptake of O_2. Interestingly, a significant enhancement in both the binding energy and adsorption capacity of O_2 was observed for UiO-66-$(OH)_2$-p, which has two -OH groups para from one another. Density functional theory (DFT) simulations were used to calculate the binding energy of oxygen to each MOF, which trended with the adsorption capacity and agreed well with the heats of adsorption calculated from the Toth model fit to multi-temperature isotherms. DFT simulations also determined the highest energy binding site to be on top of the electron π-cloud of the aromatic ring of the ligand, with a direct trend of the binding energy with low pressure adsorption capacity. Uniquely, DFT found that oxygen molecules adsorbed to UiO-66-$(OH)_2$-p prefer to align parallel to the -OH groups on the aromatic ring. Similar effects for the electron donation of the functional groups were observed for the low pressure adsorption of N_2, CH_4, and CO_2.

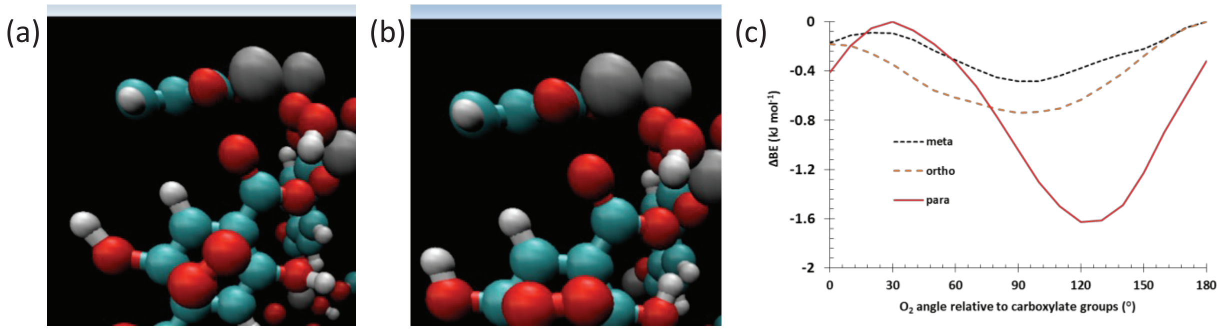

Figure: Snap shots of DFT simulations before (a) and after (b) geometry optimization of O_2 on UiO-66-$(OH)_2$-p. Plot (c) shows the change in binding energy as the O_2 molecule is rotated counter-clockwise from alignment with the carboxylic acid groups for dihydroxy linkers in the para, ortho, and meta positions.

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Novel threshold sensing architectures based on switchable MOF composites

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Threshold sensors are important elements in industrial safety systems whenever a critical MAK value (maximum permissible concentration of a substance as a gas, vapour or aerosol) or explosion limits should not be surpassed. For example for *n*-butane the lower and upper flammability limits are 1.8 and 8.4%, respectively.[1]

Metal-Organic Frameworks (MOFs) stand out in porosity and are highly selective in their interaction with gases and gas mixtures.[2] Furthermore, some of MOFs, so called *switchable* MOFs, show unique features such as *gate*-pressure behavior for specific gases, where the gas of interest can trigger a step-wise structural transition, causing a distinct volume change of the crystals.[3–5] In some cases it is accompanied also by changes in optical and magnetic properties.[5–8] Such distinct response of gating MOFs is ideal for the integration into threshold sensors. Unfortunately, no conductive switchable MOF has been reported so far, making it difficult to transferee the output to electrical signal.

Thus in order to integrate switchable MOFs into electronically addressable sensors, we have developed the synthetic route for nanostructured composite materials showing specific response towards gases at a certain threshold concentration, coupled to a pronounced change in conductivity (resistivity).

Integrated in a self-developed sensing architecture, these composites show enormous relative resistance changes during gas adsorption and can be reused at least for 10 times.

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Dualistic adsorption behavior of switchable pillar layered metal-organic framework DUT-8

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Flexible metal-organic frameworks (MOFs) or so called soft porous crystals [1] represent a subclass of MOFs that shows distinct cooperative structural transformations induced by physical or chemical stimuli resulting in a porosity switching.

Often, the phase transitions are triggered by adsorption or desorption of guest molecules and characterized by an activation energy barrier causing a hysteresis in the adsorption isotherm. Due to their capability to undergo stimulated structural transformations, soft porous crystals are often discussed as materials with huge application potential in gas separation processes, sensor technology, and catalysis [2]. However, there are still many open questions in the understanding of switching phenomena from both experimental and theoretical point of view as well as understanding of the synthesis rules, the role of the particle size, defects concentration, deviation from an ideal stoichiometry, and control over the gate pressure.

DUT-8(Ni) is one of few compounds showing either switchable or rigid behavior depending on the way it is synthesized [3-4]. This dualism in the adsorption properties allows for the investigation of factors causing and influencing particular adsorption behavior.

In situ experiments such as X-ray diffraction, EXAFS; NMR and EPR were applied to investigate structural transformations, to monitor switching during adsorption/desorption, and to get deep insights into the transformation mechanism.

We have investigated structure-property relationship between switchable and rigid DUT-8 through various spectroscopic techniques, scanning electron microscopy, elemental analysis, TGA etc. and correlated them with gas physisorption results.

Due to the fact that soft porous crystals show pronounced volume changes during the switching process resulting in high stress in the crystals, their mechanical properties and mechanism of deformation are responsible for defect formation and are important for maintaining their crystal integrity. Hence, the intriguing questions are: How stable are flexible MOFs during multiple adsorption/desorption cycles and how the mechanical stress influences the crystallite size, textural properties, and characteristic quantities of the switching phenomenon (gate opening pressure, hysteresis) during cycling adsorption experiments? Therefore, the DUT-8(Ni) was investigated using repeated adsorption of n-butane at room temperature and compared with MIL-53(Al), ELM-11, and SNU-9 [5].

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Negative Gas Adsorption in Mesoporous Switchable Metal-Organic Frameworks

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Adsorption induced stress can cause deformation of porous materials. Depending on the nature of the adsorptive, the adsorbent, and other conditions such as adsorption temperature, disordered and order porous materials can contract or expand upon guest adsorption or desorption.[1] These deformations will impact to some extent the resulting adsorption isotherm, strongly depending on the degree of deformation, which is strongly linked to the rigidity of the adsorbent. In “soft” materials such as flexible metal-organic frameworks (MOFs), large deformations are often observed leading to multiple steps and broad hysteresis in the adsorption isotherm.[2]

Recently we have reported about the new adsorption phenomenon, negative gas adsorption (NGA), which originates from a structural transition in the mesoporous MOF DUT-49 (DUT = Dresden University of Technology). Upon adsorption of gases such as methane or *n*-butane, DUT-49 contracts by over 50% in unit cell volume, reducing the pore volume of the material from 2.8 $cm^3 g^{-1}$ to 1.2 $cm^3 g^{-1}$. Along the contraction the previously adsorbed gas is expelled from the pores leading to a spike and negative slope in the adsorption isotherm. The result is a pressure amplification in the measuring cell caused by the expelled gas, counterintuitive to regular adsorption behavior.[3]

In this contribution we focus on the thermodynamic behind NGA and the techniques giving insight into the adsorption and structural behavior, such as *in situ* X-ray diffraction and *in situ* ^{129}Xe NMR spectroscopy.[4] The possibilities of manipulating and tuning the NGA, and a question whether the NGA is a generic phenomenon in porous solids or just a “whim of nature” in DUT-49 will be discussed.

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A Novel Two-Dimensional Zr-based MOF with Photoreactive Surface and its different physisorption behaviour through postsynthetic modification

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Metal-organic frameworks (MOFs) are currently one of the most investigated materials. They exhibit high specific surface areas and by using different metals and organic linker molecules tailorable properties for different applications. Especially Zr-based MOFs typically exhibit high thermal and chemical stability which is an important aspect for applications.[1]

This study describes a novel Zr-based MOF with benzophenone-4,4'-dicarboxylic acid (H_2*bzpdc*) as linker molecule. The Zr-*bzpdc*-MOF has a layered structure which exposes photochemically reactive keto-groups of the linker molecule for postsynthetic modification. Ar sorption measurements show a BET surface area of up to 650 $m^2 \cdot g^{-1}$. An Al-based MOF with this linker and the photoinduced postsynthetic modification with a small molecule inside the channels of this MOF had already described by Reinsch et al. [2] and Baldovi et al.[3] We have carried out photochemical reactions with several molecules and polymers of interest (Fig. 1).

In reactions with small molecules, all keto groups in a particle are accessed. The postsynthetic modification changes the hybridization of the keto carbon atom to sp^3, leading to minor structural changes. The intra-particle porosity is practically totally lost. With larger molecules like polyethylene glycol 300 (PEG300) or decane such trends are not observable. No structural change is visible in the PXRDs and a moderate porosity is observed (decane: 350 $m^2 \cdot g^{-1}$; PEG300: 280 $m^2 \cdot g^{-1}$). These findings indicate that with the larger molecules only the outer surface was modified. To classify up to which chain length intra-particle reaction occurs, further investigations with alkanes of different chain lengths are currently being carried out. All samples will be furthermore characterized by sorption measurements using different adsorptives. These experimental data are compared with simulated data to verify that the whole structure and the pore sizes decrease by postsynthetic modification.

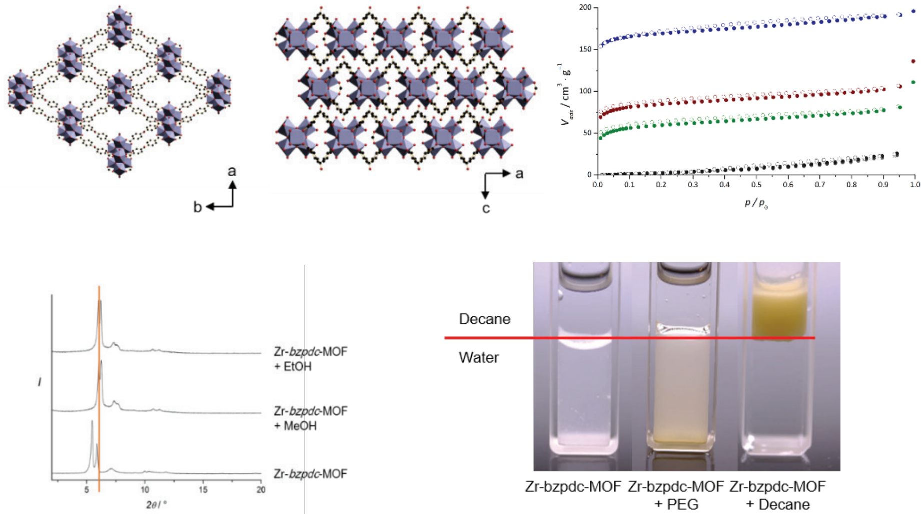

Fig 1: top left/middle: Crystal structure of Zr-*bzpdc*-MOF; top right: Physisorption measurements (N_2@77K) of the Zr-*bzpdc*-MOF (blue) and postsynthetically modified samples: methanol (grey), ethanol (black), decane (red) and polyethylene glycol 300 (green); bottom left: PXRD patterns showing a structural change of the Zr-*bzpdc*-MOF after postsynthetic treatment with small molecules (methanol and ethanol); bottom right: hydrophilic surface-modified samples of Zr-*bzpdc*-MOF: The PEG-modified sample is dispersed in the aqueous phase, the decane-modified sample in the organic phase.

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Controlled formation of hierarchical metal–organic frameworks using CO_2-expanded solvent systems

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It is shown that a crystalline metal–organic framework (HKUST-1) can be rapidly synthesized from a DMSO/MeOH solution with greatly reduced amounts of organic solvents using a supercritical CO_2 ($scCO_2$) solvent expansion technique. The precursor solution is stable for months under ambient conditions, and CO_2-driven MOF (metal–organic framework) crystallization is achieved under mild conditions (40 °C, 40–100 bar) with excellent reproducibility. As the degree of liquid-phase expansion drives MOF nucleation and growth, the crystallite size and overall yield can be tuned by adjusting the CO_2 pressure. Furthermore, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), and gas sorption analyses showed that, in the presence of $scCO_2$, HKUST-1 crystallites with a hierarchical pore structure are generated through a postcrystallization etching process. These findings demonstrate that $scCO_2$ is a time- and material-efficient route to MOF synthesis with a high level of control over the crystallization process for accessing tailored material properties.

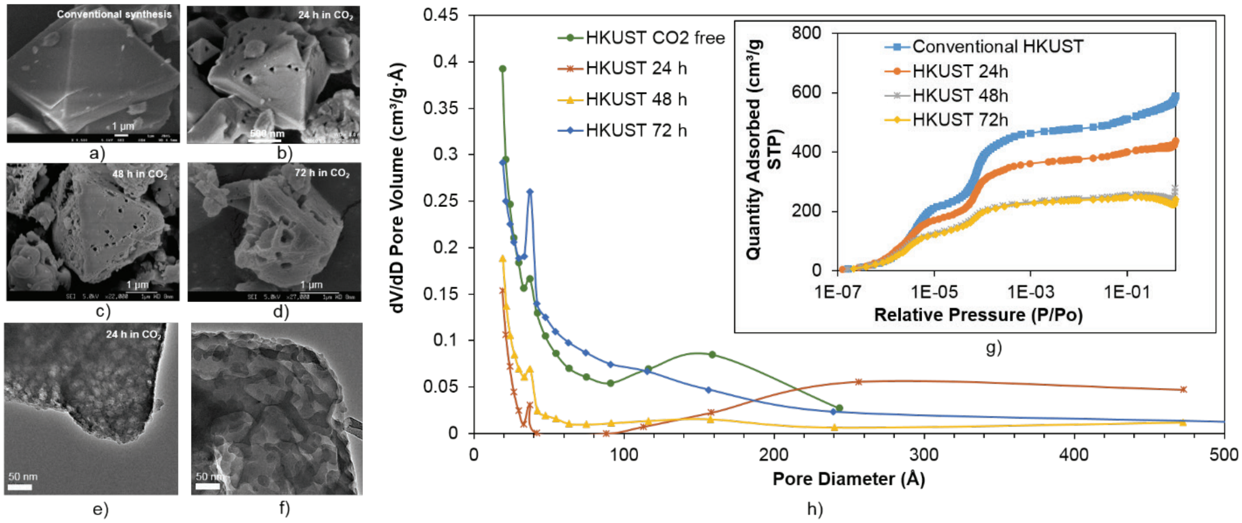

Fig. 1. SEM and HR-TEM images of HKUST-1 synthesized using different anti-solvents and reaction times (all at 40 ˚C). a) Conventional HKUST-1. b-d) HKUST-1 crystallized with 75 bar CO_2 (24, 48 and 72 hours, respectively). e and f) HR-TEM of HKUST-1 crystallized with 75 bar CO_2 over 24 and 72 hours. g and h) Gas sorption results of HKUST-1 samples precipitated with different antisolvents at varying reaction times.

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Understanding of the Gate-Opening Effect in Hydrophilic-Hydrophobic Metal-Organic Framework STAM-1

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STAM-1, a novel MOF synthetized for the first time in 2011 by Mohideen *et al.*, [1] reveals subtle flexibility of its structure combined with the presence of hydrophilic/hydrophobic one-dimensional channel system and open metal sites (**Figure 1a**). Adsorption of polar and non-polar molecules in STAM-1 was studied by the means of the QE-TPDA experimental method [2] and molecular simulation. We found that STAM-1 structure undergoes a reversible change only upon adsorption of polar molecules, *i.e. gate-opening effect* occurs, which is present on desorption/adsorption isobars of methanol (**Figure 1b**). At high temperatures the host structure is closed, and diffusion of guest molecules is not allowed, which results in zero adsorption (**1**). At 375 K (for adsorption) the molecules of methanol impose the gate opening, which can be observed as a step increase of adsorption amount (**2**). The same phenomenon takes place for desorption at 400 K, but that process runs in the opposite order. Initially the adsorbed molecules locate in the hydrophilic cavities (**3**, **Figure 1c**-bottom). Once these cavities are full, methanol is adsorbed in the hydrophobic channels too (**4**, **Figure 1c**-top).

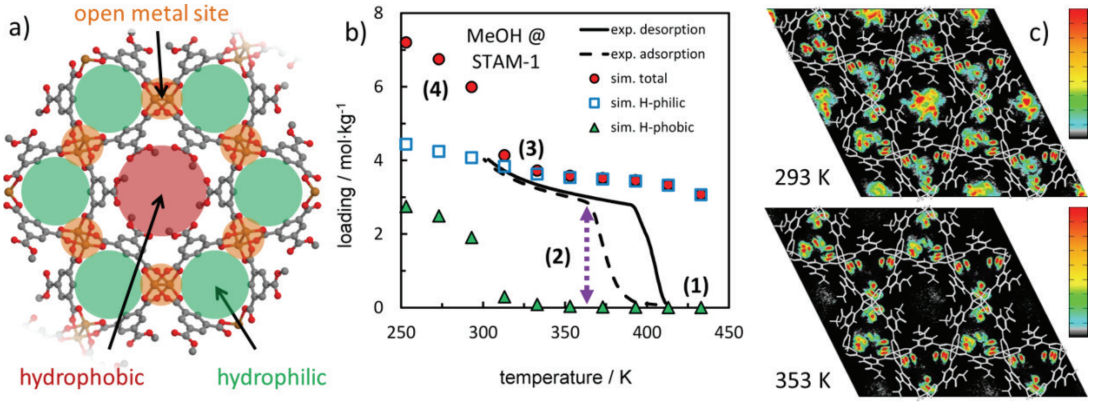

Figure 1. The scheme of the STAM-1 structure (a), experimental and calculated adsorption isobars of methanol in STAM-1 at 12.6 mbar (b), the average occupation profiles of methanol in STAM-1 (c).

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MOFs for magnetic refrigeration: Investigation of magnetocaloric effect in MOF-76(Gd)

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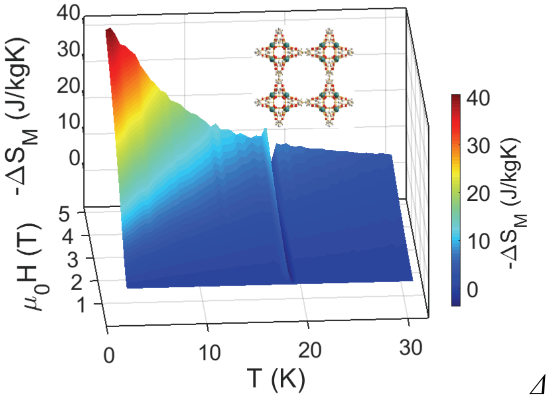
Magnetocaloric effect (MCE), as an intrinsic property of all magnetic matter, is known over century and it has been utilized in numerous applications in particular in the scope of the magnetic refrigeration. It is refereed as adiabatic temperature change induced by external magnetic field variation applied on material, what enables the cooling of materials with higher environmental and economic efficiency (in comparison with vapor-cycling technologies). Numbers of recent studies show the advantageousness of metal-organic frameworks (MOFs) in refrigeration technology and these have been found as very perspective due to their synthetic tunability and easily tailored functionality. Since MCE stems in magnetic entropy change (ΔS_M), molecular refrigerant suitable for applications should possess large spin ground state along with low-lying excited spin states, negligible magnetic anisotropy, dominant ferromagnetic exchange coupling and low molecular mass. In this context, three different MOF compounds have been prepared and characterized in the terms of magnetocaloric properties. As synthesized compound MOF-76(Gd)-DMF (**1**) with composition $\{[Gd(BTC)(H_2O)]\cdot DMF\}n$, containing DMF molecules in the cavity system, compound (**2**)$\{[Gd(BTC)]\}n$, without DMF and H_2O solvents in the cavity system, and water exchanged sample MOF-76(Gd)-H_2O (**3**). For evaluating the magnetocaloric effect (MCE), the isothermal magnetization curves *M(H)* from 1.8 to 30 K were measured using SQUID magnetometer (MPMS 5XL) and experimental data were processed employing Maxwell thermodynamic relation $(\partial M/\partial T)_H = (\partial S/\partial H)_T$. Examined MOFs compounds exhibited reasonable high values of magnetic entropy change ΔS_M varying from 31 J/kgK for MOF-76(Gd)-DMF (**1**) up to 42 J/kgK observed in for MOF-76(Gd) (**2**) at maximal field change 5 T at low temperatures. Our results confirm that the MCE effect can be tuned and controlled by exchange magnetic coupling between Gd^{3+} ions and this makes studied MOFs compounds as a promising material for magnetic refrigerator working at low temperature.



ΔS_M *vs. T* in MOF-76(Gd).

Acknowledgements:
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CPM8 | POSTER PRESENTATION

EXPERIMENTAL METHODS

Effect of shaping MOFs on adsorption performance by using adsorption microcalorimetry

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Many laboratory scale studies in the field of gas adsorption deal with as-made samples in the form of powders. However, to be of any applied use in an adsorption based process such as PSA (pressure swing adsorption), the powders need to be shaped, often in the form of spherical beads or cylindrical pellets. Nevertheless, gas separation studies using MOF pellets are still very scarce and the majority of studies concentrate on the separation performance without asking questions about the effect of the binder used or pelletization process on the fundamental adsorption properties. The effect of pelletization on the adsorption properties of the active materials should ideally be limited. Indeed, the physical properties of the material can be slightly affected as one expects a certain decrease in uptake/working capacity, proportional to the amount of binder used. However, the chemical properties which influence selectivity should remain unchanged in the presence of the binder. Other parameters such as adsorption uptake kinetics should equally remain unchanged. In this work, we have concentrated on the fundamental gas adsorption properties of several 'topical' MOFs, which not only are hydrothermally stable, cheap and easy to scale-up, but have also recently demonstrated a particular interest for gas separations. This study takes a first look at shaping on both uptakes and energies for a number of materials where the shaped material is compared with the parent powder.

Thus, a series of four Metal-Organic Frameworks (UiO-66(Zr), UiO-66(Zr)_NH_2, MIL-100(Fe) and MIL-127(Fe)) were synthesized as powders and spheres and these were characterized by gas adsorption at 30°C to 20 bars. The adsorption experiments were coupled with microcalorimetry to gain the energetic insight required to highlight any changes in chemistry. Results show that whilst most variations are as expected, interesting effects including partial pore restriction and active site 'protection' were also evidenced for some shaped materials suggesting that the binder may play a more complex role [1].

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Immersion calorimetry as a powerful tool for the characterization of MOFs

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Metal-organic frameworks (MOFs) are a relatively new class of nanoporous materials with exciting properties upon an external stimuli (for instance, upon gas adsorption, after a thermal treatment, under pressure conditions, etc.) [1]. The large potential of these crystalline structures is based on a well-defined porous structure and surface chemistry so that these properties can be easily tailored/modified by a proper selection of the organic linker and the metallic centers. One of the main issues to predict the adsorption performance of these structures is the knowledge of the porous structure (pore size and shape). Although this information can be directly extracted from the crystallographic data after appropriate fitting of the experimental data or after mathematical calculations, there are a number of case studies in the literature that reflect that this is not straightforward for MOFs. For instance, while theoretical predictions anticipate a pore size entrance below 0.34 nm for ZIF-8, experimental studies clearly show that larger molecules such as methane or nitrogen are able to access the porosity in this MOF [2,3]. A similar situation has been described recently for ZIF-7 [4]. Among the different characterization techniques available, gas adsorption (N_2) at cryogenic temperatures is the most widely used approach for the characterization of the porosity in MOFs. However, there are already a number of studies that show that nitrogen at 77K is not an appropriate choice for MOFs due to the presence of specific gas-framework interactions [5].

With this in mind, in this study we want to introduce a new characterization tool for MOFs, that is immersion calorimetry. In the absence of specific interactions, immersion calorimetry can be used for the characterization of the porous structure (pore size and shape) in MOFs. These experiments will be complemented with vapour adsorption studies using a range of hydrocarbons (linear, mono-branched and di-branched) to proof the potential of the calorimetry technique.

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REFERENCE HIGH PRESSURE CO2 ADSORPTION ISOTHERM FOR AMMONIUM ZSM-5 ZEOLITE: RESULTS OF AN INTERLABORATORY TEST

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The results of an international interlaboratory test led by the National Institute of Standards and Technology (NIST) on the measurement of surface excess isotherms for carbon dioxide adsorption on NIST Reference Material 8852 (ammonium ZSM-5) at 20 °C (293 K) are reported. Eleven laboratories participated in this exercise. Differences among the as-submitted datasets were observed, and after review of the as-submitted datasets, participants whose datasets were identified as outliers were asked to remeasure or reprocess the isotherms. Agreement in the datasets was improved when the sample was sufficiently activated and data were processed in a consistent manner. A mathematical equation is given for a fit to these isotherms, along with a 95% uncertainty interval. With the reference data derived from this exercise, this material is intended to serve as a quality-control material for the adsorption sciences. Additionally, based on lessons learned during this exercise, recommendations are made for measuring reliable high-pressure adsorption isotherms.

Adsorption of Methane on Zeolite Y: An Interlaboratory Study

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Despite major progress in adsorption technology and physical adsorption characterization during the past two decades, measurement challenges still exist for high-pressure measurements. For example, protocols for measuring high-pressure gas adsorption isotherms on well-defined porous materials have not been standardized.[1] To address these and related issues, NIST established the Facility of Adsorbent Characterization and Testing (FACT Lab). In conjunction with the Council for Chemical Research, the FACT Lab sponsored a workshop on "Measurement Needs in the Adsorption Sciences."[2] At the workshop, a recommendation was made that the adsorption science community generate reference data using existing NIST Reference Materials (RMs) through interlaboratory studies. The FACT Lab has coordinated one such study for surface excess adsorption isotherms of carbon dioxide on ammonium ZSM-5 (NIST RM 8852)[3] at 20 °C. Ten invited labs headed by experts in adsorption science participated in this study. The result was a reference high-pressure adsorption isotherm and the associated protocol for measuring isotherms.[4]

A second interlaboratory study is being launched by the FACT Lab, through VAMAS Technical Working Group № 39.[5] In this interlaboratory study, methane/zeolite Y (NIST RM 8850) surface excess adsorption isotherms will be measured up to 7.5 MPa and used to create a reference isotherm. The study will have two phases. First, participants must demonstrate their measurement capabilities, by measuring carbon dioxide/ZSM-5 reference isotherm discussed above. After this measurement capability has been demonstrated, participants will be invited to contribute to the methane/zeolite Y interlaboratory study. The contributed data will be subjected to various statistical tests to identify potential outliers,[6] after which a reference isotherm and an associated confidence interval will be extracted from the data. In addition to generating a new reference high-pressure isotherm, this study will also test the utility of the carbon dioxide/ZSM-5 isotherm for quality assurance.

This poster will present details of the new interlaboratory study and information on how to join the study.

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Dynamic and Static adsorption of carbon molecular sieves

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Gas phase and liquid phase separations using carbon particles are possible thanks to the adsorption capacity of carbonaceous materials. Recent advancements in carbon technologies allow the use of novel spherical carbon molecular sieve (CMS) particles in packed bed systems and in coated devices for analytical applications.

Spherical, high purity carbon molecular sieves were prepared from porous polymers. The carbon particles were characterized using static measurements such as low (1 bar) and high pressure porosimetry (>30 bar). Surface area was calculated from BET adsorption isotherms, and pore size and volume were calculated using Density Functional Theory (DFT) plots. Dynamic adsorption properties of the carbons were determined using chromatographic analysis in packed beds. The carbons were also characterized using TGA-MS, microscope and particle size analyses.

The static adsorption capacity of CH_4 and CO_2 on CMS particles was calculated from high pressure adsorption isotherms. Dynamic adsorption capacity was calculated using the time retention of CH_4 and CO_2 in a packed bed of carbon particles. The chromatographic analysis demonstrated significant increase in carbon dioxide retention volume when using CMS possessing a significant percentage of ultramicropores. Conversely, a CMS possessing a significant percentage of large micropores (>15Å) gave a reduced chromatographic retention volume but a large high pressure adsorption capacity. Even though some particles did not possess a large surface area (500 m^2/g), their ultramicropores provided a greater retention volume. Conversely, the CMS with a large surface area (1036 m^2/g) and large pore volume provided the greatest static capacity using high pressure adsorption for carbon dioxide.

The data obtained indicate surface area is not sufficient to predict the applied CMS performance. Additional properties (i.e., pore diameter) are required to design adsorption processes since different kinetic modes may benefit from different structural carbon parameters.

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Isosteric heat: comparative study between Clausius-Clapeyron, CSK and Cal-Ad methods

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In this work the isosteric heat was determined using several methods reported in literature for five prepared,samples which had different textural and chemical characteristics. The samples used were: graphite, MOF-199, SBA-15, activated carbon obtained from corn cob and zeolite. The methods that were used to evaluate isosteric heat were: Clausius-Clapeyron method (CC) [1], the method developed by Chakraborty et.al [1,2] (CSK), and the direct method by Adsorption Calorimetry (Cal-Ad) [3], which were compared to each other and the obtained results were discussed.

The studied solids have surface areas between 5 and 1450 $m^2.g^{-1}$. Each of these samples presented very different textural and chemical properties, because of that it was associated with the results obtained in the determination of the isosteric adsorption heats.

The isosteric heats evaluated presented very different behaviors for each analyzed sample. In this work the values obtained by adsorption calorimetry were higher compared to those calculated by the C-C and CSK methods. This work presents the results obtained and their respective analyzes according to the thermodynamic principles of each applied model.

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Low temperature Dynamic Quantum Molecular Sieving of Oxygen Isotopes using one-, two- and three-dimensional nanoporous materials

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Isotope molecules play crucial role for various advanced technologies including isotope labelling, renewable energy, nuclear power and medical diagnostic applications. Recently, ^{18}O a stable isotope of oxygen has been extensively utilized for isotopic labelling to elucidate various reaction mechanism in chemistry, metabolic pathways and transport mechanism in living organisms and for nuclear medical imaging Positron Emission Tomography (PET). More particularly, it can act as a target in cyclotron for producing [^{18}F]-labeled 2-deoxyglucose (FDG) as β-emitting radioisotope for PET biomedical imaging technique. The PET imaging or a PET scan can show abnormalities which other techniques may not detect, resulting in early and more accurate diagnosis of the infected (tumor) body cell [1,2]. Consequently, ^{18}O isotopes has shown escalating increasing demand over last decade. However, the natural abundance of ^{18}O is only up to 0.204 at. %. So, in order to meet the demand of sustainable society with this inadequate accessibility, an advanced, cost-effective separation method is the need of time. However, the present techniques for oxygen isotope separation suffer from inherent inadequacy related to high energy consumption, prolonged processing time and very low separation factor (max.～1.0406 for NO distillation) [3], consequently extremely high cost. Recently, low temperature adsorption based quantum molecular sieving (QMS) of lighter isotopes using nanoporous adsorbents has been represented as the most promising avenue to substitute primitive separation methods. The QMS involves relatively simple separation mechanism based on reversible physisorption in confined system which account for their short processing time and high selective separation [4-6]. In this report, we are presenting highly selective low temperature adsorption based quantum molecular sieving separation of $^{18}O_2$ from a mixture of $^{18}O_2$-$^{16}O_2$ gases using 1-D (oxidized single walled carbon nanotube; ox-SWCNT), 2-D (Activated carbon fibers; ACFs, carbide derived carbon; CDC) and 3-D (zeolites) porous adsorbent materials. The high separation factor using quantum molecular sieving effect in the nanoporous adsorbents will open a promising avenue for the $^{18}O_2$ isotope harvest for advancements in biomedical applications particularly PET.

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In-depth investigation of the closed porosity of glassy carbons by scattering techniques

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Non-graphitic carbons (NGCs) represent important carbon materials. Linking their intrinsic (micro)porosity to the sp^2-polyaromatic microstructure, especially analyzing the degree of disorder's impact on porosity, is crucial to understand effects of different precursors and carbonization temperatures. However, distinguishing between open porosity, contributing to adsorption ability and closed porosity is essential.
Here, we analyze glassy carbons based on phenolic resin heat-treated at different temperatures (800 °C - 3000 °C) by small angle neutron scattering (SANS) as well as wide X-ray scattering (WAXS) techniques. We determine different structural parameter describing the carbon microstructure and the porosity. We use the concept of the "chord-length distribution (CLD)" to analyze the data, which provides useful structural parameters describing the pore space. For instance, the value of the g(r) at $r = 0$ give information of the angularity of the pores respectively the shape of the pores, and the first moment of the CLD (Porod length lp) is correlated to the average pore size and average wall thickness. Furthermore, we determine the porosity by analyzing the absolute intensity of the SANS curves (Figure 1), too. The volume fraction P of the pores contributing to the observed small-angle scattering was calculated. Microstructural parameter like the average graphene layer size L_a and the stacking height L_c are determined by an advanced algorithmic method for the structural characterization of non-graphitic carbons. We address the question, if there is a correlation between the pore size and the stacking height determined by WAXS (Figure 1). All in all, an in-depth quantitative comparison of the pore structure based on parameters like the Porod length l_p, the average pore size $<l_p>$, the correlation length l_c, the wall size $<l_{matter}>$, the specific internal surface S, the volume fraction P and the polydispersity of the chord-length k_c is shown.

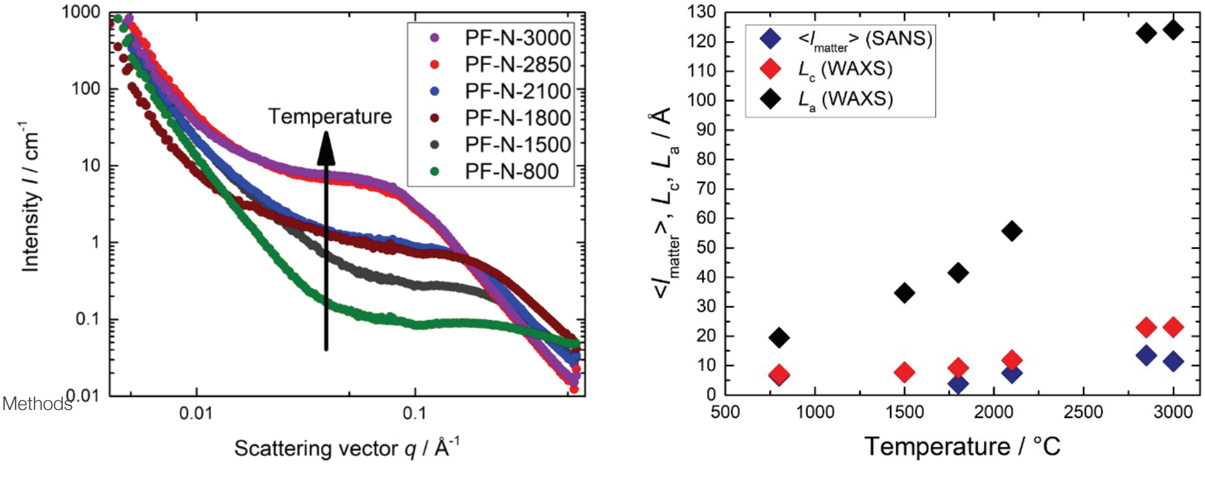

Figure 1. SANS curves of the glassy carbon samples (left) and the graphene layer size L_a (black), stacking height L_c (red) and the size of the pore walls $<l_{matter}>$.

Following adsorption of water and hydrogen in porous materials – formation of hydrogen bonds and cooperative effects

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The adsorption of liquid and gasses, particularly hydrogen and water, is important for many areas of science and applications ranging from energy storage for hydrogen economy to transport phenomena in geology and biology. In this context, the understanding of hydrogen bonds formation in various environment and criteria governing the molecular mobility at nanoscale is of high importance. Using neutron scattering as a powerful magnifying glass and gradually changing the amount of adsorbed molecules we have investigated molecular structure and dynamics of hydrogen and water in pores of different sizes. By an aimed selection of the confining systems, we were able to systematically follow the molecular behavior in in environments with variable degrees of guest-host interactions. We observe that in systems with weak guest-host interactions the molecular mobility depends non-linearly from the confinement size. With an increase of guest-host interactions, we see the onset of adsorption induced changes of the host structure and the formation of new structural phases of guest molecules. These molecular scale phenomena ultimately control macroscopic properties such as sorption storage capacity, isotherm behavior etc.

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Cycling Experiments in Microporous Carbon Adsorbed Natural Gas Tanks

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The search for cheaper and cleaner automotive fuels has driven the study of carbon based adsorbed natural gas (ANG) tanks, for next-generation clean vehicles [1-6]. Storage of methane in such a tank is fully reversible under the standard fill/discharge protocol: pressurization to 35 bar or higher at ambient temperature to fill the tank (adsorption); depressurization to 2 bar or higher at ambient temperature to empty the tank (desorption) [5]. But storage of natural gas, consisting of approximately 90% methane and 10% non-methane components, is reversible only in part under this protocol. Co-adsorbed non-methane components, depending on their binding energy on the adsorbent and kinetic factors, are released only in part under the stated discharge conditions and therefore will accumulate in the tank during successive fill/discharge cycles, reducing the amount of useable fuel stored in the tank over time. A typical value for retention of non-methane components is 2 mass% per fill/discharge cycle [6, 7]. Normally, to restore the full fuel storage capacity of the tank, the tank is heated off-board under vacuum for a prolonged period of time (regeneration, forced desorption of non-methane components) [8]. One proposed way to eliminate the need for off-board regeneration is to add an on-board fuel extraction system [9], in which a compressor provides suction on the tank, upstream of the compressor, and enhanced fuel flow to the engine, downstream of the compressor. We tested the effectiveness of such a system, for extraction of non-methane components, on the 40-liter flat-panel ANG tank at the University of Missouri [5]. We ran 20 fill/discharge cycles and monitored the mass of the tank and composition of the discharged gas as a function of time over the 20 cycles. The mass of the full tank (35 bar) and mass of the empty tank (2 bar) both increased with increasing cycle number, n, but the fuel delivered in cycle n, mass(full, n) – mass(empty, n), decreased with increasing n. In as few as five cycles, n = 5, the tank capacity mass(full, n) – mass(empty, n) had dropped by over 2.5% from the “pristine capacity” mass(full, 1) – mass(empty, 1). The increase in empty-tank mass, mass(empty, n) – mass(empty, 1), gives the mass of non-methane components that remain in the tank after n cycles, and the ratio [mass(empty, n) – mass(empty, 1)]/”pristine capacity” gives the fraction of non-methane components in the tank after n cycles. This ratio was 0.9 kg/3.4 kg for n = 5. Thus, already after 5 cycles, the tank holds 26% non-methane components. This rapid decrease in fuel delivered and rapid increase of non-methane components suggests that the compressor does not eliminate the need for periodic regeneration of the tank. However, the two metrics considered here for successful forced fuel extraction, do not grow linearly with n but approach constant values for large n. We will discuss to what extent the approach to such constant values can be treated as reversible storage, but with reduced capacity compared to storage of pure methane.

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Control of Mechanical Stability of Hollow Silica Particles, and Its Measurement by Mercury Intrusion Porosimetry

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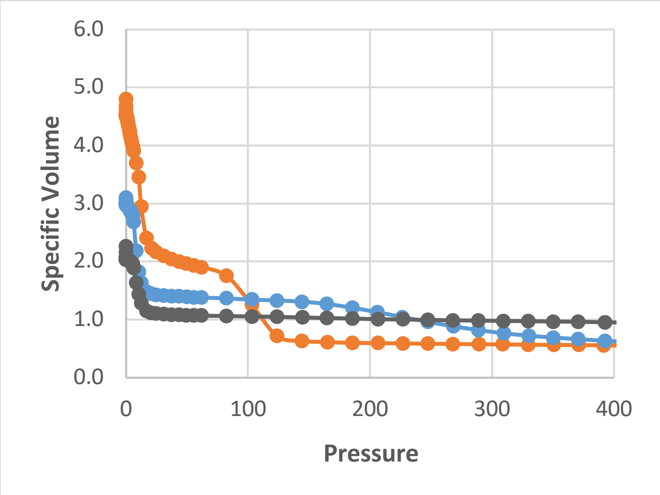
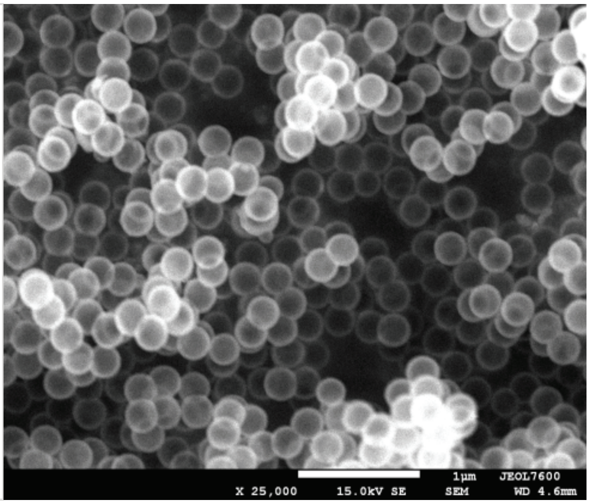
Hollow silica particles (HSPs) have become the focus of interest in many labs recently, due to their versatility, stemming from the ability to control their size and shape, as well as surface functionalization. Determining the mechanical stability of hollow particles is essential for their use, both in applications in which they need to retain their structure, as well as those in which they need to break down. We have synthesized a series of HSPs with different wall thickness, using a template approach. Their mechanical stability was measured using mercury porosimetry, which, to the best of our knowledge, represents the novel application for these materials. Other characterization methods, namely microscopy, gas adsorption, and small angle X-ray scattering shed light on the particles' size parameters, as well as the porosity of the silica walls. By varying the amount of silica precursor used in the template coating step, we were able to produce hollow silicas with variable stability, thereby allowing for the design of their mechanical properties.





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Pore-scale ink flow in thin coating layer of paper

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Coated paper are used in inkjet printing industry in order to control ink flow and produce high print quality. The coating layer is usually a thin-porous layer of $CaCO_3$ with thickness of 15 um and mean pore size of 180 nm. Imaging and reconstruction of the layer was done previously using focused ion beam scanning electron microscopy (FIB-SEM) [1]. In this work, pore-scale two-phase flow simulation of water-based ink in the layer was done using direct simulation methods. A detailed ink flow pattern inside layer was resulted and then validated by ASA measurement and FIB-SEM results. Results showed a penetration depth of 25 um and spreading length of 50 um for a droplet of 30 pL. Addition of 50% glycerol to the model ink showed optimum penetration and spreading extends which consequently resulted in better print quality. The developed modeling method can be used in study of ink flow and change in its properties on final print quality. Furthermore, the developed imaging and modeling methods can be used in general for various type of fluid flow in thin porous coating layers with micro and meso-scale pore sizes.

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Digital Rock Physics: Segmentation Comparison for a Carbonate Rock

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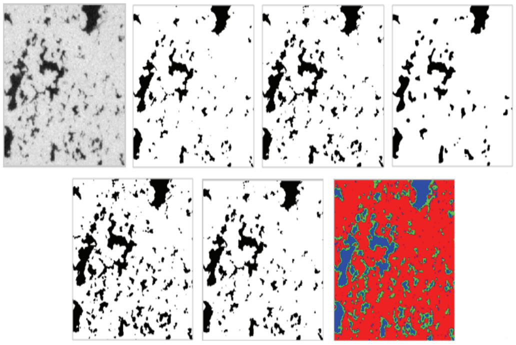
The main workflow of DRP involves three steps; image acquisition, image segmentation and numerical computations[6], [7]. Image acquisition can be done via any of the available imaging technologies such as X-ray computed tomography (XCT) that allow for the non-invasive imaging of the core plug to resolutions down to the micron range[8]. Image segmentation is the separation of the image into discrete phases – usually the pore space as well as one or more solid phase depending on the type of mineralogy of the sample. The segmentation stage is crucial for DRP as it could alter the results of numerical simulations. In this work, a systematic study was conducted where different segmentation techniques were applied to determine their effect on porosity and permeability values. Images of a carbonate rock were acquired from a 0.5 inch diameter cylindrical core sample at a resolution of 13.24 micrometer using a micro-CT. Even though the image dataset acquired was of the size of 1004x1024x1995voxels, for the purpose of this study, a cubic subvolume of size 300^3 voxel was extracted. Following that, five segmentation algorithms were studied;



Segmentation	Total Porosity	Effective porosity	Permeability (D)
Interactive Thresholding – Low	0.0977	0.0372	0.134
Interactive Thresholding - High	0.138	0.113	0.592
Watershed	0.103	0.039	0.2125
Tophat and watershed	0.167	0.153	1.7116
Otsu	0.138	0.113	0.5954
K-means	0.0845	No connection	No connection

Figure 1. [From left to right] (a) Original Image (b) Minimum thresholding (c) Maximum thresholding (d) Watershed (e) Watershed and Tophat (f) Otsu (g) K-means

As shown in the table of figure 1, segmentation results show that the total porosity, effective porosity and permeability can vary greatly depending on the segmentation type used. While Otsu's algorithm gave similar results to the manually selected thresholding technique on the high side, the rest fell into two extremes; with k-means, manual (low) threshold and watershed on the lower end, and watershed with top hat on the upper end. The range of permeability spans from "no connectivity" to a 1.71 Darcy permeability.

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Mineralogical alterations in calcite powder flooded with $MgCl_2$ to study Enhanced Oil Recovery (EOR) mechanisms at pore scale

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Seawater injection into chalk-reservoirs on the Norwegian Continental Shelf has increased the oil recovery and significantly reduced seabed subsidence, but not eliminated it. Understanding rock – fluid interactions at micro- and nano-scale is paramount in up-scaling optimized water injection in the field and to predict and control water induced compaction, being pivotal in all our modeling exercises.

In-house laboratory experiments on onshore and reservoir chalks have shown the need to simplify the aqueous chemistry of the injected brine, and more recently also the importance of studying the effect of primary mineralogy of chalks flooded in order to understand which ions in seawater interact with the minerals present. In this study not only the ionic composition of the injected brine, but also the original mineralogy of the samples tested, are simplified. In chalk reservoirs, the non-carbonate minerals may vary from a few to 15 wt.%. The experiments are carried out on pure calcite powder (99.97 % $CaCO_3$), compressed to cylinders (d~3.7 cm, L~7.0 cm), flooded with $MgCl_2$, in tri-axial cells, at 130°C and 0.5 MPa effective stress. During these short and long-term experiments, ranging from 27 to 289 days, any ionic changes of the effluent with time were logged.

After each flooding experiment, the calcite was analyzed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM), Transmission Electron Microscopy (TEM), and whole-rock geochemistry, using ICP-MS technique. The results show a transformation from calcium- to magnesium-carbonate, identified as magnesite, with minor impurities of calcium, through dissolution and precipitation. The occurrence and shape of new-grown crystals depend on flooding time and distance from the inlet of the cylinder. Crystals vary in shape, from nanometers up to 1-2 μm after only 27 days, while may grow to over 10 μm after 289 days of flooding (Figure 1 a and c). Away from the inlet (~3 cm) in the same test, an intermediate stage of smaller magnesite crystals clustered in cauliflower-like shapes are found (Figure 1b).

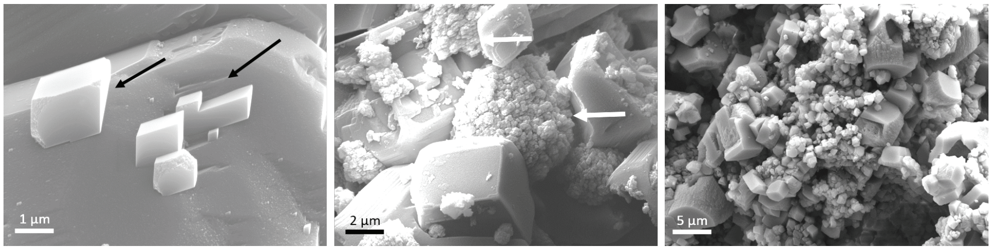

Figure 1: Newly formed magnesite on calcite grains after flooding with $MgCl_2$. Arrows: magnesite crystals. a) Up to micron-sized crystals growing after 27 days. b) Intermediate phase of clusters of smaller magnesite crystals in 289-days test ~ 3 cm from the inlet. c) Magnesite crystals of varying size at inlet of the test in b) with seemingly no calcite left.

Our new findings on calcite powder can be used to simulate single-grain growth, and compared with in-house experiments on chalks with varying non-carbonate content, these studies allow for a more detailed insight of where, when and, how these crystals preferentially grow. Further investigations will define the exact preferred growth of secondary minerals on primary ones to gain even more information on how rock-fluid interactions affect compaction, porosity, and permeability evolution, hence production of oil.

Nanoparticle separation on polymer-grafted porous substrates

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We explore interactions of functionalized nanoparticles (NP) with polymer brushes (PB) in a binary solvent that is a mixture of good and bad solvents. Varying the solvent composition causes PB to expand or contract and to regulate the effective affinity of NPs to PB. The NP adhesion is also affected by the surface properties of NPs that can be tuned by functionalization. NP-PB systems appear in multiple applications, and our interest here is to utilize the specifics of NP-PB interactions in the chromatographic separation of NPs with respect to their surface chemistry. This separation can be achieved by NP flow through polymer-grafted porous columns where the micro-channel walls are covered by PBs. Using dissipative particle dynamics simulations in conjunction with the Ghost Tweezers free energy calculation technique, we examine the free energy landscape of functionalized NPs in a PB-grafted channel depending on the solvent composition, nature of the NP functionalization, grafting density, and chain length. NP-PB adhesion is governed by the affinity of polymer chains to NP surface relative to the solvent and entropic repulsion caused by polymer chain confinement between NP and channel wall. The former depends on surface chemistry of NPs while both factors depend on solvent composition. Using the calculated free energy profiles we determine the probability of NP location at given distance to the surface and then analyze NP transport through a polymer-grafted channel to calculate the mean velocity of NPs as a function of NP size and solvent composition. We find[1] that with the increase of the bad solvent fraction, NP separation exhibits a transition from the hydrodynamic regime with larger NPs having shorter retention time to the adsorption separation regime with smaller NPs having shorter retention time. This transition is reminiscent to the critical condition in polymer chromatography, implies that NPs of similar surface properties can be separated independent of their size, and has important practical implications: NPs can be separated by surface chemistry rather than by their size. We further analyze the effects of NP surface properties on this transition by studying interactions of NPs functionalized with two types of ligands. Our simulations show that the transition point, indicated by a particular solvent composition, depends strongly on the ligand composition on the NP surface, which further supports the possibility of separating them according to their surface properties using the gradient mode of chromatography.

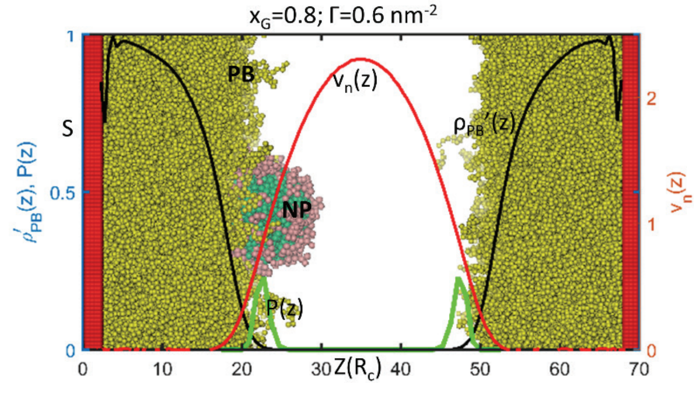

Figure 1. Schematics of NP flow in PB-grafted channel. PB density profile shown by black, solvent velocity distribution profile shown in red, NP location probability shown in green. The substrate is shown in red, polymer beads in yellow, NP beads in green and ligand beads in pink.

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CPM8 | POSTER PRESENTATION

DYNAMICS, DIFFUSION, AND DEFORMATION

Determining Mechanical Properties on Different Structural Levels by Adsorption-Induced Deformation

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Analysis of adsorption-induced strain measured in-situ, e.g. in parallel to an adsorption isotherm or just as a function of relative pressure, is a powerful tool to access mechanical properties such as the Young's modulus or the modulus of compression on different structural levels of a porous structure. Experimental techniques typically applied to obtain the strain data are in-situ dilatometry and in-situ small angle scattering (small angle X-ray (SAXS) or neutron scattering (SANS)). In both cases, the sample is subject to stress initiated by adsorption on the microscopic scale of the material, while the resulting strain is monitored by a method either probing the strain on the microscopic scale (small angle scattering) or accessing the macroscopic deformation of the porous structure (dilatometry). Earlier approaches used parts of strain isotherms in the region beyond capillary condensation to estimate elastic constants [1,2]. Combining the two experimental methods [3] applied to different types of silica based model systems with refined theoretical modeling [4], we provide a first quantitative approach using the full strain isotherms for the mechanical analysis of porous solids that do not contain micropores. We illustrate how the Young's modulus of the nonporous backbone and the effective mechanical properties of a mesoporous phase can be determined from the experimental strains even in solids with hierarchical porosity, where the macroscopically accessible modulus is determined by both, the properties of the mesoporous phase and the structural characteristics of the macropores. The applied approach allows investigation of highly ordered as well as disordered isotropic porous solids. The mechanical properties extracted are consistent with other methods, e.g. the determination of the bulk Young's modulus by sound velocity measurements or the respective value for a nonporous silica backbone as derived via inelastic neutron scattering.

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Acknowledgements:

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Assessing Adsorption-Induced Deformation in Hierarchical Porous CMK-3-Type Carbon Materials

Lukas Ludescher[1,2], Roland Morak[1], Christian Balzer[3], Stefan Braxmeier[3], Florian Putz[4], Michael Elsässer[4], Gudrun Reichenauer[3], Nicola Hüsing[4], Oskar Paris[1] and Gennady Y. Gor[2]

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Adsorption induced deformation (AID) takes place in all micro- and meso- porous materials and is a promising mechanism for actuators and sensing devices. The proliferation of devices based on this idea is hindered, in particular, due to a limited theoretical understanding of adsorption induced deformation. Although qualitative understanding of the physical principles has advanced in the last years, quantitative models of adsorption induced deformation are rather limited[1]. Most of these advances were made in materials exhibiting slit or cylindrical pores[1], but not much has been published on the deformation of pores with other geometries.

In this work we present an approach to quantitatively describe AID on materials that are formed by a system of parallel rods with adsorption taking place on a convex surface. The samples investigated were hierarchically structured porous carbons exhibiting a disordered macropore structure, a CMK-3 like structure on the mesopore level and different amounts of micropores induced by activation. The mean distance between the hexagonally arranged carbon rods was measured with in-situ small angle neutron scattering (SANS) as a function of the relative pressure of the chosen adsorptive n-pentane. Furthermore, from the incoherent scattering background we determine the amount adsorbed in-situ[2].

We describe the adsorption isotherm with a geometrical approach[3] to understand the capillary condensation in a system of hexagonally arranged cylinders. Further, we calculate the capillary pressures between the cylinders with an analytical model and compare these findings with the experimental data from SANS. Hence, this study represents a new approach to describe adsorption deformation phenomena quantitatively for open, convex pore systems.

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Multifaceted Experimental Study of Molecular Diffusion and Transport through Nanoporous Alumina

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Understanding transport phenomena in porous catalysts is key to optimizing yield and minimizing costs in a vast array of processes. Transport properties depend on a large amount of factors such as the topology (including porosity, tortuosity and connectivity), the molecule/pore size ratio and surface interactions such as adsorption among others. This study aims to use complementary experimental techniques to develop a predictive model that can provide quantitative information on said transport and adsorption properties in alumina-based catalysts, widely used in industry (for example in the notably complex hydrotreatment processes in petroleum refineries).

Inverse size exclusion chromatography (ISEC) technique, was used to characterize alumina samples by injecting polymers of different hydrodynamic radii and analyzing their journey through the porous network via their chromatographic peaks - smaller molecules penetrate further into the smaller pores, thus taking more time to navigate the medium, while larger molecules traverse much faster through the interparticular porosity.[1] Experiments were first performed in non-adsorbing conditions in order to strictly isolate the transport phenomena, which allows for a topological characterization of the medium. Adsorbing conditions (through the use of a different solvent) must then be employed to account for the adsorption process in a non-activated support. This adds a new layer of information - the surface diffusion phenomenon. The ISEC technique allows for two different and complementary approaches known as the dynamic and static methods [2], both relying on different experimental procedures and different terms of the van Deemter equation.

Electrical tortuosity measurements were performed on the alumina samples using the dilution method for powders [3] and a new method to measure the longitudinal and radial tortuosities in anisotropic materials such as monoliths. Along with mercury porosimetry, the tortuosity experiments were carried out to confirm the results obtained by the in-situ ISEC techniques on both commercially available as well as home-made chromatographic columns and monoliths. All these mutually corroborating methods help to introduce material structure parameters into a global model that can better predict the transport properties within porous materials.

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Active Behavior of Graphene Nanowindow Rims

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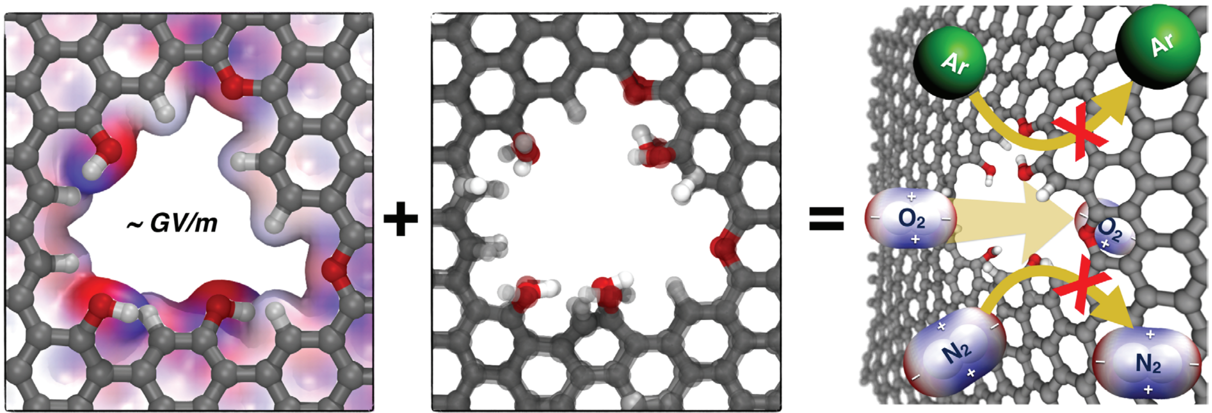
Graphene with nanoscale windows (nanowindows) can become the most selective, fastest and energy-efficient membrane for molecular separations. This nanowindow is not electrically neutral due to passivation of the carbon edges under ambient conditions, becoming a flexible atomic framework with functional groups along its rim.

We will show that during adsorption at equilibrium conditions, graphene nanowindows can actively store dipolar- and quadrupolar-interacting molecules. This is due to the large electrostatic field on its vicinity, even though no surface exists. This makes the nanowindow act as a quasi-wall for selective molecular adsorption.

Also, through computer simulations of O_2, N_2 and Ar permeation, we reveal the remarkable nanowindow behavior at the atomic scale: (i) flexible nanowindows have thousand times higher permeability than conventional membranes and at least twice its selectivity for O_2/N_2 separation. (ii) molecules 10% larger than a nanowindow easily permeate due to the concerted rim motion and short-lived transition state; (iii) an intra-nanowindow electrostatic field of GV/m order accelerates molecular permeation of electrically-interacting molecules, and (iv) weakly interacting functional groups open/close the nanowindow with their thermal vibrations to selectively control permeation. This selective ultra-fast permeation of O_2, N_2 and Ar in very restricted nanowindows contributes in designing the new generation of air separation membranes.

Graphene nanowindows are charged, flexible and selective



Electrostatic field created by functional groups

Concerted thermal vibrations

Selective (O_2/N_2=20) and ultrafast (10 kGPU) permeation

Determination of gas diffusivity in alumina porous materials using Flux Response Technology

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We characterize gas diffusivity in alumina samples with various pore structures using flux response technology (FRT), aiming to reveal relationship between the pore characteristics of the material and its mass transport properties, and thus to suggest hints for improving design of catalyst reactors.

Three types of alumina (α, γ, θ) were processed by jet-mill technology to controllably modify particle size with minimal effect on pore structure. FRT methodology, developed based on a pneumatic Wheatstone bridge assembly that enable high sensitivity of changes in gas flow as described in previously published works [1, 2]. Six samples (names in caption of Fig 1) with different pore structures (not shown here) were examined for diffusion of propane (C_3H_8). Except sample A, all samples were prepared into particles of 600 μm in diameter, applying pressure of about 80MPa in 10 min, and then crushed.

As shown in Fig 1, gas diffusivity values obtained for samples B through E are similar in the range of 10^{-11} m^2 s^{-1}. The lowest value for sample A (α-Al_2O_3) is predicted as this sample does not contain primary pores. The similar diffusivity for other samples may be partially explained by the fact that all these samples were pelletized at high pressure, which narrowed the micro-pores, making the samples to have similar pores.

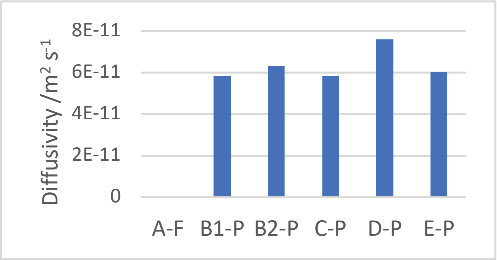

Fig 1 Gas diffusivity in alumina samples with different pore structures, estimated in FRT experiments

Pore structure in materials has great impact on gas transport, and thus influences catalytic performance of the materials.

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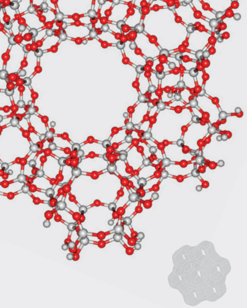

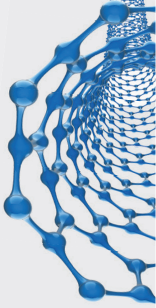

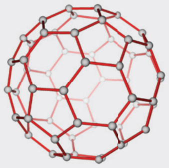

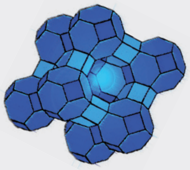

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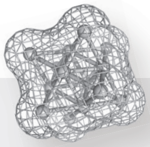

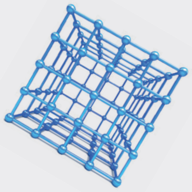

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