Ninth International Workshop
"Characterization of Porous Materials: From Angstroms to Millimeters"

May 19 – May 22, 2024

Workshop Chair: Alexander V. Neimark
Rutgers University, USA

Workshop Vice-Chair: Matthias Thommes
Friedrich-Alexander University Erlangen-Nürnberg, Germany

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 the journal "Adsorption".

Special sessions will focus on:

- Novel Nanoporous Materials and Adsorption Processes for Industrial Applications
- Computational Design and Screening of Novel Adsorbents
- Modeling and Characterization of Hierarchical Nanostructured Materials
- Adsorption Induced Deformation and Phase Transformations of Porous Frameworks
- In-situ Monitoring of Adsorption and Fluid Flow in Porous Structures
- Adsorption and Characterization of Geosorbents: Shale, Coal, Soil
- Adsorption of Polymers, Proteins, and Nanoparticles on Porous Substrates

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

International Advisory Committee

Australia

Paul A. Webley, Monash University

Austria

- Freddy Kleitz, University of Vienna

Argentina

- Karim Sapag, Universidad Nacional de San Luis

Belgium

- Joeri Denayer, Vrije Universiteit Brussel

Brazil

- Diana Azevedo, Federal University of Ceara. Fortaleza
- Fred Tavares, Federal University of Rio de Janeiro

France

- Benoit Coasne, University of Grenoble-Alpes, France
- Renaud Denoyel, Aix-Marseille University-CNRS
- Alain Fuchs, Paris Science and Letters

Germany

- Michael Fröba, University of Hamburg
- Martin Hartman, Friedrich-Alexander-University Erlangen-Nürnberg
- Stefan Kaskel, Technische Universität Dresden

Greece

- Theodore Steriotis, NCSR Demokritos
- Pantelis N. Trikalitis, University of Crete

Japan

- Katsumi Kaneko, Shinshu University
- Hirotomo Nishihara, Tohoku University

Morocco

- Youssef Belmabkhout, Mohammed VI Polytechnic University, Benguerir

Poland

- Bogdan Kuchta, Wrocław University of Science and Technology

Portugal

- Paulo Mota, Universidade NOVA de Lisboa

Spain

- Joaquin Silvestre-Albero, University of Alicante

UK

- Stefano Brandani, University of Edinburgh
- Marc-Olivier Coppens, University College London
- Erich Muller, Imperial College London
- Lev Sarkisov, University of Manchester

USA

- Teresa Bandosz, City College, New York
- Keith Gubbins, North Carolina State University
- Peter Ravikovitch, ExxonMobil, Annandale, NJ
- Randy Snurr, Northwestern University, Evanston, IL
- Krista Walton, Georgia Institute of Technology

From the Organizers

On behalf of the Organizing Committee, we would like to welcome the advisory committee members, lecturers, and participants of the 9th International Workshop "*Characterization of Porous Materials: from Angstroms to Millimeters*" – CPM-9 in Delray Beach, Florida, USA, on May 19-22, 2024.

CPM-9 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, 2015, and 2019. Following our tri-annual schedule, CPM-9 should have been held in 2021. However, due to the Covid-19 pandemics, we had to postpone CPM-9 until 2024. 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 18 countries from five continents, CPM-9 is one of the central international events in the subject area in 2024.

The CPM-9 program features 9 invited keynote lectures, 37 oral presentations, and 70 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 include regular, disordered, and hierarchical nanostructured materials used as adsorbents, catalysts, drug carriers, and membranes, as well as natural nanoporous systems like shale, coal, and other geomaterials.

After the conclusion of the CPM-9 program on Wednesday afternoon, May 22, our local sponsor Anton Paar QuantaTec will host a barbeque lunch and a lab tour of their facilities in nearby Boynton Beach.The CPM-9 papers selected through a rigorous peer-review process will be published as a Special Issue of Adsorption, the journal of the International Adsorption Society, following a tradition of previous CPM meetings, 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, and Microporous and Mesoporous Materials, V. 304, 2020.

The submission website will be open and ready for article submission at the Springer Nature system on May 31, 2024, at https://link.springer.com/journal/10450. To access the submission portal, please visit the main journal web page and click at "Submit your manuscript". To ensure that all manuscripts are correctly identified for inclusion into the special issue, it is important to select the Special Issue title under the "Details" tab, in the "Collection" drop-down menu. 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 submission guidelines posted on the journal website. The deadline for manuscript submission is August 31, 2024. Papers accepted for publication will be continuously published online and the Special Issue web page will gradually be filled. We expect the CPM-9 Special Issue to be completed around January 2025.

We are looking forward to an exciting and fruitful meeting.

With warm wishes,

Alex Neimark, Workshop Chair	Matthias Thommes, Workshop Co-Chair
Rutgers University	Friedrich-Alexander University
Piscataway, New Jersey	Erlangen-Nürnberg, Germany

Sunday, 19 May, 2024

4:00pm – 6:00pm Registration

6:00pm – 8:00pm Welcome Reception

Monday, May 20, 2024

8:30am – 8:40am Welcome Address

Alex Neimark and Matthias Thommes

8:40am – 9:00am Opening Remarks

Katsumi Kaneko, Shinshu University, Japan

Session 1: Adsorption and Transport

Session Chair: José Paulo Mota

9:00 – 9:30	***Keynote:* Adsorption and diffusion in nanoporous materials: the view from the nanoscale** Benoit Coasne CNRS/Univ. Grenoble Alpes
9:30 – 9:50	**Rapid Characterization of Mass Transfer in Fiber Composites Using a Commercial Volumetric Adsorption Instrument** Kaihang Shi, Florencia Son, Randall Snurr, Omar Farha University at Buffalo, State University of New York
9:50 – 10:10	**Shell-Core Structure in Extruded Pellets Characterized Using the Zero Length Column Technique** Stylianos Kalaitzopoulos, Enzo Mangano, Stefano Brandani University of Edinburgh
10:10 – 10:40	Coffee Break

Monday, May 20, 2024 Session 2: Experimental Methods I Session Chair: Teresa Bandosz	
10:40 – 11:10	*Keynote:* **Deformation Dynamics of Nanoporous Solids upon Liquid Imbibition** Juan Sanchez, Patrick Huber Hamburg University of Technology and Deutsches Elektronen-Synchrotron DESY
11:10 – 11: 30	**Topological cluster structure of water confined in hydrophobic pores** Yasuhiro Sugiyama, Ryusuke Futamura, Taku Iiyama Shinshu University
11:30 – 11: 50	**Quantitative Assessment of Hydrophilicity/Hydrophobicity in Nanoporous Materials** Carlos Cuadrado Collados, Alexandra Inayat, Ana-Sunčana Smith, Dorothea Wisser, Jakob Söllner, Jan Paul Grass, Martin Hartmann, Matthias Thommes, Rustam Durdyyev FAU Erlangen-Nürnberg, Erlangen, Germany
11:50 – 12:10	**Investigating preferential adsorption of N2 from the air in Zeolite 13X using total neutron scattering** Daniel Bowron, Marta Falkowska The University of Manchester
12:10 – 12:30	**Selectivity in adsorption of responsive metal-organic frameworks** Irena Senkovska, Leila Abylgazina, Mariia Maliuta, Stefan Kaskel, Volodymyr Bon Dresden University of Technology
12:30 – 2:00	Lunch Break

Monday, May 20, 2024 Session 3: Molecular Simulations Session Chair: Guillaume Maurin	
2:00 - 2:30	***Keynote:* Insights into Capillary Condensation and Hysteresis in Nanoporous Materials from New Simulation Methods** Randall Q. Snurr, Zhao Li, Filip Formalik, Jesse Prelesnik, and J. Ilja Siepmann Northwestern University
2:30 – 2:50	**Anomalous interaction between propylene and Ag cation in zeolites** Hideki Tanaka, Tomoki Ogata, Motomu Sakai, Masahiko Matsukata, Katsuya Teshima Shinshu University
2:50 – 3:10	**Unusual coexisting adsorption and structural transformations mechanism in Nano-Porous Materials** Bogdan Kuchta Wroclaw University of Science and Technology, Department of Chemistry
3:10 – 3:30	**Understanding the Origins of Reversible and Hysteretic Pathways of Adsorption Phase Transitions by Mesocanonical Ensemble Monte Carlo Simulations** Shivam Parashar, Alexander Neimark Rutgers University
3:30 – 3:50	**Flat-histogram Simulations of Water in MOFs: Advanced Strategies for Overcoming Sampling Challenges** Daniel Siderius, Harold Hatch, Vincent Shen National Institute of Standards and Technology
3:50 – 4:10	**Mechanism of Vapor Sorption and Sorption-Induced Deformation in Bacterial Spores** Gennady Gor, George Scherer, Howard Stone Princeton University, NJIT
4:30 – 7:00	Poster Session with Refreshments (Coffee/ Beer/ Hors d'oeuvres) **Session Chairs: Daniel Siderius and Gennady Gor**

	Tuesday, 21 May, 2024 Session 4: Experimental Methods II Session Chair: Stefano Brandani
8:00 – 8:30	***Keynote:* Combining multiple functions to achieve process intensification in adsorptive separations** Joeri Denayer, Mohsen Gholami, Ravi Sharma, Matthias Schoukens, Gille Wittewrongel, Rahul Maity Vrije Universiteit Brussel
8:30 – 8:50	**Measurement of multicomponent adsorption isotherms based on a temperature-step approach and mass spectrometry** Nicolas Chanut, Robbe Van Loenhout, Cesar Para Cabrera, Masaya Sugihara, João Fernandes, Margot Verstreken, Leen Boullart, Rob AMeloot KU Leuven
8:50 – 9:10	**Direct visualization of Al distribution inside zeolite crystals** Yoshihiro Kamimura, Tetsuya Kodaira, Akira Endo National Institute of Advanced Industrial Science and Technology
9:10 – 9:30	**Predicting the pore-structure transport relationship in disordered alumina using hyperpolarized xenon MRI and NMR cryodiffusometry** Stefano Marc Collins, Sean Rigby, Huw Williams, Galina Pavlovskaya, Thomas Meersmann, Arthur Harrison, Christophe Vallée, Thibaud Chevalier, Dina Lofficial University of Nottingham and IFP Energies Nouvelles
9:30 – 9:50	**Kinetic measurements on monoliths using the Adsorption Differential Volumetric Apparatus (ADVA)** Enzo Mangano, Riccardo Rea, Mohsen Gholami, Joeri Denayer, Stefano Brandani The University of Edinburgh
9:50 – 10:10	**Towards “infinite” selectivities in CO2/CH4 and CO2/N2 separations with MgNa-GIS flexible zeolite** Remy Guillet CNRS - LCS
10:10 – 10:40	Coffee Break

Tuesday, May 21, 2024 Session 5: Computational Design of Nanoporous Materials Session Chair: Randy Snurr	
10:40 – 11:10	***Keynote:*** **Material discovery with physics and AI** Lev Sarkisov The University of Manchester, UK
11:10 – 11: 30	**Dissemination and updates to the universal standard archive file for adsorption data** Daniel Siderius, Jack Evans, Stefan Kaskel Fraunhofer IWS & TU Dresden
11:30 – 11: 50	**Applications of 3D Amorphous Carbon Molecular Models for Adsorption and Mechanical Property Predictions** Nicholas Corrente, Elizabeth Hinks, Aastha Kasera, Raleigh Gough, Peter I. Ravikovitch, Alexander Neimark Rutgers University
11:50 – 12:10	**Computational-aided development of MOF-based Mixed Matrix Membranes for molecular separation** Guillaume Maurin Université Montpellier/CNRS
12:10 – 12:30	**Molecular Simulation of Peptide Retention in Reversed-Phase Liquid Chromatography** José Paulo Mota NOVA School of Science and Technology
12:30 – 2:00	Lunch Break

<table>
<tr><th colspan="2">Tuesday, 21 May, 2024
Session 6: Experimental Methods II</th></tr>
<tr><td>2:00 - 2:30</td><td><i>Keynote:</i> Structural changes in ZIFs upon gas and liquid phase adsorption
Joaquin Silvestre Albero
University of Alicante</td></tr>
<tr><td>2:30 – 2:50</td><td>On the characterization of nanoporous carbons with small-angle scattering
Oskar Paris, Christian Prehal
Montanuniversität Leoben</td></tr>
<tr><td>2:50 – 3:10</td><td>Use of Ultrasonic Monitoring for In situ Diagnostics of Zeolite and MOF Crystallization
Martin Hartmann, Hasan Baser, Marcus Fischer, Rebecca Reber, Wilhelm Schwieger
Erlangen Center for Interface Research and Catalysis, FAU Erlangen-Nürnberg, Erlangen, Germany</td></tr>
<tr><td>3:10 – 3:30</td><td>Correlations of NMR Relaxometry Data and Polymer Surface Chemistry
Alan Allgeier, Murilo Suekuni
University of Kansas</td></tr>
<tr><td>3:30 – 3:50</td><td>Advanced Textural and Surface Chemistry Characterization by Combining Adsorption and Liquid Intrusion with NMR Relaxometry
Carola Schlumberger, Carlos Cuadrado Collados, Jakob Söllner, Lukas Sandner, Jincheng Xu, Matthias Thommes
Institute of Separation Science and Technology, Friedrich-Alexander-University Erlangen-Nuremberg</td></tr>
<tr><td>3:50 – 4:10</td><td>Brain Tissue Modeled as a Porous Medium with parameters derived from Micro-Iontophoresis Experiments
Charles Nicholson
NYU School of Medicine</td></tr>
<tr><td>4:10 – 4:40</td><td>Coffee Break</td></tr>
</table>

Tuesday, 21 May, 2024 Session 7: Theoretical Methods Session Chair: Benoit Coasne	
4:40 – 5:10	*Keynote:* **3-D Density Functional Theory to Describe Adsorption of Pure Substances and Their Mixtures on Crystalline and AMorphous Adsorbents** Frederico Wanderley Tavares Universidade Federal do Rio de Janeiro
5:10 – 5:30	**A non-local Density Functional Theory for water adsorbed in nanoporous materials.** Antoine Barthes, David Grégoire, Christelle Miqueu Université de Pau et des Pays de l'Adour
5:30 – 5:50	**Coupling between poroelasticity and the density functional theory for the estimation of adsorption-induced swelling in nanoporous materials** David GREGOIRE, Youssef Khaldouni, Laurent Perrier, Thomas Bernet, Christelle Miqueu Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France
5:50 – 6:10	**Framework-dependent kinetics of adsorption-induced structural transition in flexible metal-organic frameworks** Shotaro Hiraide, Yuta Sakanaka, Iori Sugawara, Hajime Uematsu, Shogo Kawaguchi, Minoru Miyahara, Satoshi Watanabe Kyoto University
6:10 – 6:30	**Impact of a kerogen network on the behavior of confined hydrocarbon liquids** Bennett D Marshall, Dmitry N. Lapshin, Erich A. Muller, Peter I. Ravikovitch Imperial College London
8:00	Conference Dinner

<table>
<tr><th colspan="2">Wednesday, 22 May, 2024
Session 8: Experimental Methods III
Session Chair: Oskar Paris</th></tr>
<tr><td>8:30 – 9:00</td><td><i>Keynote:</i> Structure characterization-mediated designing of novel carbon-based nanostructured materials
Katsumi Kaneko
Research Initiative for Supra-Materials, Shinshu University</td></tr>
<tr><td>9:00 – 9:20</td><td>Designing Macroporous-Mesoporous Adsorbents for Sustainability
Freddy Kleitz, Aaron Brewer, Changxia Li, Patrick Guggenberger, Justyna Florek
University of Vienna, Austria</td></tr>
<tr><td>9:20 – 9:40</td><td>Tuneable mesoporous silica materials for gas storage applications via nanoconfined clathrate formation
Pegie Cool
University of Antwerp</td></tr>
<tr><td>9:40 – 10:00</td><td>Effect of surface chemical heterogeneity of carbon textiles on their detoxification activity against CWA surrogate
Marc Florent, Paola S Pauletto, Teresa J Bandosz
CCNY</td></tr>
<tr><td>10:00 – 10:20</td><td>Adsorption separation of CO2 from CH4/CO2 mixture by Low Silica X zeolite and Recovering of Adsorption Heat for Further Applications
Akihiko MATSUMOTO, Keiichi Hasegawa, Yuji Hasegawa
Toyohashi University of Technology</td></tr>
<tr><td>10:20 – 10:50</td><td>Coffee Break</td></tr>
</table>

Wednesday, 22 May, 2024 Session 9: Nanomaterials for Adsorption Applications Session Chair: Martin Hartmann	
10:35 – 11:20	***Keynote:*** **Separation Performance of Zeolitic-Imidazolate-Framework-Based Membranes** Michael Tsapatsis John Hopkins University
11:20 – 11:40	**Unique characterization data of graphene mesosponge** Hirotomo Nishihara Tohoku University
11:40-12:00	**Formation and Characterization of ZIF-8 Supraparticles and Their Packings with Hierarchical Porosity** Satoshi Watanabe, Atsushi Fujiwara, Minoru Miyahara, Nicolas Vogel, Shotaro Hiraide Department of Chemical Engineering, Kyoto University
12:00 – 12:20	**Functional porous physisorbent materials from phosphorite waste: Advanced characterizations and applications** Ali Mohammed YIMER, Ayalew Hussen ASSEN, Youssef BELMABKHOUT Mohammed VI Polytechnic University
12:20 – 12:40	**Porous silica-coated magnetic nanoparticles for molecular diagnostics of virus infection** Adriana Zelenakova Pavol Jozef Šafarik University in Košice
12:40 – 1:00	**CPM9 Closing:** **Concluding Remarks** Keith Gubbins North Carolina State University, USA **Closing Ceremony** Alex Neimark and Matthias Thommes
1:30	**Barbecue lunch and company tour of Anton-Paar QuantaTec in nearby Boynton Beach** (Transportation Provided)

CPM9 | POSTER PRESENTATION

1. ***Temperature-Dependent V-Type Isotherm Models: Applied to Water Vapor Adsorption on Metal-Organic Frameworks***
   Cristian Cardenas
   IFP Energies Nouvelles
2. ***Facile Characterization of Pore Accessibility in Metal-Organic Framework/Polymer Composites***
   Trenton Tovar
   U.S. Army, DEVCOM Chemical Biological Center
3. ***Characterization of hydroxyl groups in zeolite defects using advanced temperature-programmed desorption***
   Shunsuke Shimizu, Hirotomo Nishihara, Ryota Osuga, Takeharu Yoshii
   Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
4. ***High sensitivity analysis of nitrogen in carbon materials using temperature-programmed desorption up to 2100 °C***
   Takeharu Yoshii, Ginga Nishikawa, Hirotomo Nishihara
   Tohoku University
5. ***Explorations of the Molecules-to-Materials Continuum***
   Robert Szilagyi
   The University of British Columbia - Okanagan
6. ***Characterization of Mycelium-Based Leather Using Sorption-Ultrasonic Experiments***
   Gunel Nabiyeva, Ashoka Karunarathne, Christopher Rasmussen, Naila Assem, Jonathan Bauer, Alexei Khalizov, Gennady Gor
   Dept. of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, NJ, USA
7. ***Validation of pore size distribution from a new GCMC kernel based on a slit-pore model with carbon surface heterogeneity***
   Kazuyuki Nakai
   MicrotracBEL Corp.
8. ***Kinetics of Adsorption-Induced Deformation in Microporous Materials***
   Andrei Kolesnikov, Gennady Gor
   Department of Chemical and Materials Engineering, New Jersey Institute of Technology
9. ***Sorption-Ultrasonic Characterization of Water-Filled Xerogels***
   Ashoka Karunarathne, Alexei Khalizov, Gennady Gor, Gudrun Reichenauer, Stephan Braxmeier
   New Jersey Institute of Technology
10. ***Assessment of the Specific Surface Area by Small-Angle X-ray Scattering***
    Andreas Keilbach, Armin Moser, Heike Ehmann
    Anton Paar GmbH

11. ***Extruding diffusion constants from your extrudates: PFG-NMR and chromatography***
    Sean Mclntyre, Daryl Williams, Paola Sáenz-Cavazos, Paul IACOMI
12. ***Impact of Crystal Structure on Methanol Vapor Adsorption in MFI-Type Zeolites: Equilibrium Isotherms and Kinetic Insights***
    Coset Abreu Jauregui, Francisco Murilo Tavares de Luna, Igor de Mesquita Figueredo, Joaquín Silvestre-Albero, Leandro Martins
    University of Alicante
13. ***Quantification of Copolymer Microstructure from Liquid Chromatography using a Statistical Interaction Model***
    Christopher Rasmussen, Yefim Brun
    Bolt Threads Inc.
14. ***Estimation of porous media transport properties solely based on mercury intrusion porosimetry***
    David Grégoire, Gilles Pijaudier-Cabot, Fadi Khaddour, Lionel Ecay, Sara Khalil
    Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France
15. ***The influence of confinement effects on the thermophysical properties of 4-methoxyazobenzene***
    Timm Kraus, Michael Fröba
    Universität Hamburg
16. ***PyCOSMOS: A Python Tool for Compartmentalization of Unit Cells of Metal-Organic Frameworks***
    Shivam Parashar, Alexander Neimark
    Rutgers University, New Jersey, USA
17. ***Modelling Kerogen Flexibility in Response to Hydrocarbon Adsorption using Hybrid Molecular Dynamics/Monte Carlo***
    Shivam Parashar, Alexander Neimark, Peter I. Ravikovitch
    Rutgers University, New Jersey, USA
18. ***Characterization of Nanoporous Carbons Using Generative Models***
    Lucas J. Santos, Elvis do A. Soares, Amaro Gomes Barreto Jr., Frederico Wanderley Tavares
    Universidade Federal do Rio de Janeiro
19. ***A Novel Method for Obtaining Carbon Molecular Sieves for N2/O2 Separation***
    Koki Urita, Kaito Marubayashi, Miyu Hamasaki, Hideki Tanaka, Takashi Ishida, Yasuyuki Yamane, Jin Miyawaki, HIroo Notohara, Isamu Moriguchi
    Nagasaki University
20. ***INFRAsorp & MULTIport Rapid surface analysis by optical calorimetry***
    Stefan Kaskel, Felix Spranger
    Fraunhofer IWS; TU Dresden
21. ***Unique dissolution/precipitation phenomena in microspace induced by physisorption***
    Takeru Yokoyama, Taku Iiyama, Ryusuke Futamura, Takahiro Ueda, Yuka

Matsuda
Faculty of Science, Shinshu University 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan

22. ***Reference Isotherms for Water Vapor Sorption on Nanoporous Carbon: Results of an Interlaboratory Study***
Huong Giang Nguyen, Blaza Toman, Roger van Zee, Matthias Thommes
National Institute of Standards and Technology
23. ***Small-angle neutron scattering reveals high-density adsorbed hydrogen in carbon micropores at low pressures and supercritical temperature***
Sebastian Stock, Malina Seyffertitz, Nikolaos Kostoglou, Max Valentin Rauscher, Bruno Demé, Christian Mitterer, Oskar Paris
Montanuniversität Leoben, Chair of Physics
24. ***Scalable Continuous Flow Hydrogenation Using Structured Catalyst Reactor***
Andrea Adamo, James Mannino, John Holcombe, Lorenzo Milani, Steve Stark, Vladimiros Nikolakis
W.L. Gore & Associates Inc.
25. ***Solid-State Hydrogen Storage: Advancements in Nanoporous Materials and Neutron Scattering Techniques***
Haihua Wang, Mi Tian, Oana Ghita, Valeska Ting, Xiayi Hu
University of Exeter
26. ***Microscopic understanding of stability and adsorption/separation of CO2 from flue gas by MOFs in real industrial conditions***
M. Wahiduzzama, P. Lyu, N. Heymans, N. Garcia-Moncada, G. Mouchaham, M. Daturi, G. De Weireld, C. Serre, Sabine Devautour-Vinot, G. Maurin
ICGM CNRS/ENSCM/UM
27. ***Understanding wetting and drying of nanoporous media through optical and dilatometry experiments***
Juan Sanchez, Laura Gallardo, Yannick Tetzner, Patrick Huber
Hamburg University of Technology
28. ***CH4/H2O Competitive adsorption in Nano porous materials under clathrate hydrate formation conditions***
JYOTI SHANKER PANDEY, Joaquin Silvestre Albero
DTU CHEMICAL ENGINEERING
29. ***Acoustic Response of Fluid Adsorption in Nanoporous Materials***
Loriane Didier, Alan Sam, Rodolfo Venegas, Benoit Coasne
CNRS/Univ. Grenoble Alpes
30. ***Supercritical fluid activation and in-situ adsorption-microcalorimetric system to directly measure the gas adsorption amount, heat and kinetic data***
Wentao Jiang, liuliu long, Yue-Biao Zhang
ShanghaiTech University
31. ***Evaluation of a Commercial Chabazite-Type Zeolite Aging in the Industrial Process of Dehydration of Natural Gas CO2-Enriched***

Kalil Kashefi, Marcos Anacleto da Silva, Vera M.M. Salim, Frederico W. Tavares, NEUMAN SOLANGE DE RESENDE, Amaro G. Barreto
Universidade Federal do Rio de Janeiro, EQ

32. ***Reference Isotherms using Reference Materials***
Roger van Zee, Blaza Toman, Huong Giang Nguyen, Matthias Thommes
NIST
33. ***Converting Waste Tire to Activated Carbon Adsorbent Materials for Landfill Gas Purification***
Brandyn Nutter, Amirjavad Ahmadian Hosseini, Laura Rojas, Masoud Jahandar Lashaki
Florida Atlantic University
34. ***Improving the robustness and reproducibility of gas adsorption isotherm measurements on nanoporous materials***
Darren Broom
Hiden Isochema Ltd
35. ***Densification and Validation of Binderless MOF Monoliths Based On Temperature-Pressure Swing Hydrogen Storage and Delivery Conditions***
Ruthradharshini Murugavel, Ali Rownaghi, Fateme Rezaei
Department of Chemical & Biochemical Engineering, Missouri University of Science and Technology
36. ***Self-template Synthesis of Nanoporous Carbons from π-conjugated Ionic Liquids with Molecular Nanocarbon Functionalities***
Ryusuke Futamura, Toshinori Seki, Kento Nakamura, Ryuta Sekiguchi, Taku Iiyama
Shinshu University
37. ***Investigating the effect of the extra-framework cation on propane / propylene adsorption in LTA zeolites***
Claessens Benjamin, Emily Bloch, Gabriel Trierweiler-Conçalves, Gerald Chaplais, Jean Daou, Jean-Louis Paillaud, Mohammed-El Amine Benchaabane, Sandrine Bourrelly
Aix-Marseille University, CNRS
38. ***Carbon Dioxide Capture in NaOH-Impregnated Activated Carbon***
Prapatsorn Borisut, Atichat Wongkoblap, Chaiyot Tangsathitkulchai, Aroonsri Nuchitprasitchai, Krittamet Phothong
Suranaree University of Technology
39. ***Metal Organic Framework Hollow Fibers for CO2 adsorption and Chemical Warfare Agent Degradation***
John Landers
Apollodyne
40. ***Hydrophobic metal-organic frameworks with new fluorinated ligands***
Vladimír Zeleňák, Dávid Princík, Adriána Zeleňáková
Faculty of Natural Science, Pavol Jozef Safarin University in Kosice, Slovakia

41. ***Development of novel porous geopolymer monoliths based on Moroccan oil shale for effective removal of heavy metals (Zn (II), Cu (II), Pb (II)) from wastewater.***
    said mansouri, SANAE SBI, JONES ALAMI, HASSAN HANNACHE, YOUSSEF TAMRAOUI
    Mohammed VI Polytechnic University, Benguerir
42. ***Sorption of SF6 and SO2 on Modified Zeolites Materials***
    Katarzyna Zarębska, Mikihiro Nomura, Megumi Irie, Jakub Szczurowski
    Faculty of Environmental Engineering, Geomatics and Renewable Energy, Kielce University of Technology, 25-314 Kielce, Poland
43. ***Trapped in the CO2 Loop: A Study of Carbon/MOF Composites for Direct Air Capture (DAC)***
    Jakub Szczurowski, Adrian Lubecki, Katarzyna Zarębska, Patryk Bartulik
    Faculty of Environmental Engineering, Geomatics and Renewable Energy, Kielce University of Technology, 25-314 Kielce, Poland
44. ***Applications of MOFs for the chemical warfare agents (CWAs) simulant adsorption***
    Emily Bloch, Guillaume Maurin, Lotfi Boudjema, Sandrine Bourrelly
    Aix-Marseille University - CNRS MADIREL
45. ***3D-printed hybrid zeolite structures constructed by a phase inversion process***
    Ben Sutens, Marleen Rombouts, Steven Mullens, Yoran De Vos
    VITO
46. ***Novel nanoporous composites for hydrogen storage***
    Alex Pennetier, Jean-Philippe Torré, Laurent Perrier, Christelle Miqueu
    Université de Pau et des Pays de l'Adour
47. ***In situ pXRD monitoring of compliant MOFs under combined mechanical and gas pressure***
    Paul IACOMI, Pascal Yot, Christian Serre, Frederico Alabarse, Sujing Wang, Guillaume Maurin
48. ***Impact of Carbon Content in Single-Wall Carbon Nanotube-Titanium Dioxide Composites Interfacial Modulation and Catalytic Behavior***
    Coset Abreu Jauregui, Antonio Sepúlveda-Escribano, Joaquín Silvestre-Albero
    University of Alicante
49. ***Tailoring the Adsorption Properties of Hierarchical Porous Silicas for High-Capacity Water Sorbents***
    Pasquale Fulvio, JiaJi Lin, Krista Walton
    Georgia Institute of Technology
50. ***Quantifying Structural Rigidity in Metal–Organic Frameworks with Increased Linker Dimensionality***

Courtney Smoljan, Omar Farha, Randall Snurr
Northwestern University

51. ***Carbon Dioxide Capture from Flue Gas using 13X binder free Zeolite: effect of the presence of Sulfur Dioxide***
Celio Cavalcante, Diana Azevedo, Enrique Vilarrasa-Garcia, Eurico Torres, Moises Bastos-Neto, Rafaelle Santiago
Universidade Federal do Ceara
52. ***A Comparative Study of Physical and Chemical Modification for Improved CO2 Capture in Fixed-Bed Adsorption***
Suravit Naksusuk
School of Chemical Engineering, Suranaree University of Technology
53. ***Analyzing the Performance of Propylamine-Grafted Mesoporous Silica for Direct Air Capture Applications***
Amirjavad Ahmadian Hosseini, Laura Rojas, Masoud Jahandar Lashaki
Florida Atlantic University
54. ***Triamine-Grafted Mesoporous Silica Materials for CO2 Capture from the Atmosphere***
Laura Rojas, Amirjavad Ahmadian Hosseini, Masoud Jahandar Lashaki
Florida Atlantic University
55. ***Molecular mechanisms of water intrusion and extrusion in hydrophobic nanopores***
Abdelraheem Abdella, Kolattukudy P. Santo, Alexander Neimark
Rutgers, The State University of New Jersey
56. ***Molecular simulation of separation of C60 and coronene in silica nanopores***
Rustam Durdyyev, György Hantal, Ana-Sunčana Smith
PULS Group, Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute for Theoretical Physics, Interdisciplinary Center for Nanostructured Films
57. ***Composite Boron Nitride-based Immobilized Nanohydride Toward Self-Accelerated Reversible Hydrogen Storage***
Maxwell Tsipoaka, Fateme Rezaei
Missouri University of Science and Technology
58. ***The Effect of Carbon Nanotube Diameter on Hydration of Critical Material Ions from E-waste***
Qing Shao, Zachary Baker
University of Kentucky
59. ***Mechanical Properties of Gases Adsorbed in Micropores from the Fluctuation Theory***
Santiago Flores Roman, Alina Emelianova, Gennady Gor
New Jersey Institute of Technology

60. ***Molecular Simulation of Adsorption of Sarin and Simulants on Metal–Organic Frameworks***
Elizaveta Basharova, Alina Emelianova, Allen Reed, Gennady Gor, Andrei

Kolesnikov
New Jersey Institute of Technology

61. ***A unified approach for bridging the gap between cDFT and equation of state for confined fluids***
    Amaro Gomes Barreto Jr., Dárley Carrijo de Melo, Felipe Rocha Pinto, Frederico Wanderley Tavares, Vítor Sermoud
    Universidade Federal do Rio de Janeiro
62. ***Hydrogen storage: predicting at room temperature in a series of activated carbons***
    José Carlos Alexandre de Oliveira, Daniel V. Gonçalves, Sebastião M. P. Lucena
    Universidade Federal do Ceara
63. ***Study of Crystallization Pressure by Molecular Simulation***
    Bilal MAHMOUD HAWCHAR, Laurent brochard, Florian osselin, Jean-Michel Pereira, Matthieu Vandamme, tulio honorio
64. ***Incorporating material flexibility effects into adsorption modeling using non-local Density Functional Theory***
    Christelle Miqueu, Raphael Labeyrie
    Université de Pau et des Pays de l'Adour
65. ***Modeling Adsorption of Simple Fluids and Alkanes on 3D Nanoporous Carbons***
    Nicholas Corrente, Elizabeth Hinks, Aastha Kasera, Raleigh Gough, Peter I. Ravikovitch, Alexander Neimark
    Rutgers University, New Jersey, USA

66. ***SAFT-DFT Studies of Nanoporous Carbon Deformation Induced by Multicomponent Adsorption***
    Nicholas Corrente, Elizabeth Hinks, Aastha Kasera, Alexander Neimark
    Rutgers University, New Jersey, USA
67. ***Development and application of an advanced percolation model for pore network characterization by physical adsorption***
    Jakob Söllner, Alexander Neimark, Matthias Thommes
    Institute of Separation Science and Technology, Friedrich-Alexander Universität Erlangen-Nürnberg

CPM9 | REPORT OF ABSTRACTS

MONDAY, MAY 20, 2024

Adsorption and diffusion in nanoporous materials: the view from the nanoscale

Benoit Coasne[1]

[1] Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France

Email for correspondence: benoit.coasne@univ-grenoble-alpes.fr

Nanoporous materials (pore size 1–100 nm) are at the heart of numerous important applications: adsorption (e.g. gas sensing, chromatography), energy (e.g. hydrogen storage, fuel cells and batteries), environment (e.g. phase separation, water treatment, nuclear waste storage), etc. Among these materials, nanoporous solids which have pores $\lesssim$ nm (e.g. active carbons, zeolites), are particularly interesting as ultraconfinement in their porosity leads to novel adsorption and transport phenomena. Thorough understanding of these effects and the underlying molecular mechanisms is critically needed to better characterize nanoporous solids. In this talk, I will present how statistical physics allows developing models for adsorption and transport in these extremely confining materials [1,2]. We will see how simple thermodynamic modeling allows rationalizing adsorption by considering reminiscent capillarity at vanishing lengthscales. Then, we will show how transport in subnanoporous media can be described without having to rely on macroscopic concepts such as hydrodynamics [3,4,5]. In particular, using parameters and coefficients available to experiments, we will see how transport coefficients can be rigorously upscaled using simple models such as free volume theories, etc. I will also briefly illustrate how the confinement of fluids in metallic nanoporous materials departs from what is observed for insulating materials [6].

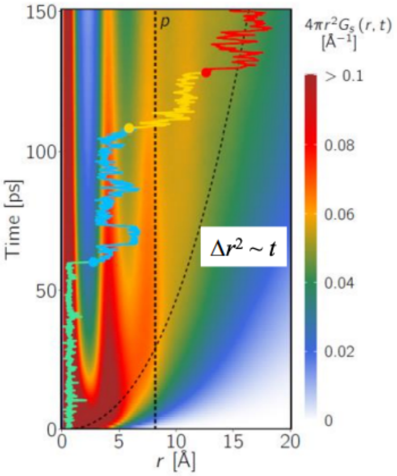


Figure 1. Propagator Gs(r,t) [prob. that a molecule is translated by a quantity r over a time t] for a Lennard-Jones fluid confined in a nanoporous carbon (From Ref. [5]).

References:

1 B. Coasne et al., Chem. Soc. Rev. 42, 4141 (2013).
2 I. Deroche et al., Nature Comm. 10, 4642 (2019).
3 K. Falk et al., Nature Comm. 6, 6949 (2015)
4 T. Lee et al., Nature Comm. 7, 11890 (2016)
5 C. Bousige et al., Nature Comm. 12, 1043 (2021).
6 A. Schlaich et al., Nature Materials 21, 237 (2022).

Rapid Characterization of Mass Transfer in Fiber Composites using a Commercial Volumetric Adsorption Instrument

Kaihang Shi,*†,[1,2] Florencia A. Son, †,[3] Randall Q. Snurr,*[1]and Omar K. Farha*[1,3]

[1] Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, 60208, United States
[2] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York, 14260, United States
[3] Department of Chemistry and International Institute for Nanotechnology, Northwestern University, Evanston, Illinois, 60208, United States
†Equal contribution from both authors
Emails for correspondence: kaihangs@buffalo.edu; snurr@northwestern.edu; ofarha@northwestern.edu

MOF/fiber composites have shown much promise as protective equipment for the capture and remediation of chemical warfare agents. However, the practical application of these composites requires an understanding of their mass transport properties, as both mass transfer resistance as the surface and diffusion within the materials can impact the efficacy of these materials. Experimental characterization of molecular transport typically requires specialized and expensive facilities, such as confocal Raman microscopy or infrared Raman microscopy, which – although they provide beneficial insights – suffer from limited accessibility, inhibiting the development of new applications of porous materials.

In this talk, we present a new Fickian diffusion model to quantitatively characterize the surface permeation and in-pore diffusion of molecules in MOF/fiber composites having cylindrical shapes. The new diffusion model takes input data from a commercial volumetric adsorption instrument, which is readily accessible in most laboratories compared to other specialized facilities for studying molecular diffusion. Using this newly developed method, we were able to study the mass transport of n-hexane and 2-chloroethyl ethyl sulfide (CEES) in composite fibers of MOF-808 and functionalized polymers of intrinsic microporosity. We found that transport in these materials is dominated by surface barriers, and diffusion within the bulk of the composite materials is fast in comparison. These preliminary insights and the model introduced in this work lay the groundwork for the design of next-generation composite materials for practical applications.

References:

1. F.A. Son†, K. Shi†, R.Q. Snurr, O.K. Farha, Mass Transport of n-Hexane and 2-Chloroethyl Ethyl Sulfide in Fiber Composites of MOF-808 and Amidoxime-Functionalized Polymers of Intrinsic Microporosity, in preparation.

Acknowledgements:

O.K.F. and R.Q.S. gratefully acknowledge support from the Defense Threat Reduction Agency (HDTRA1-19-1- 0007). F.A.S. is supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate (NDSEG) Fellowship Program and the Ryan Fellowship through the International Institute for Nanotechnology at Northwestern University. K.S. gratefully acknowledges the start-up support from the University at Buffalo.

Shell-Core Structure in Extruded Pellets Characterized Using the Zero Length Column Technique

Stylianos Kalaitzopoulos[1], Enzo Mangano[1], Stefano Brandani[1]

[1] School of Engineering, Institute for Materials and Processes, University of Edinburgh, The King's Buildings, Edinburgh, EH9 3FB, UK

Emails for correspondence: e.mangano@ed.ac.uk, s.kalaitzopoulos@sms.ed.ac.uk, s.brandani@ed.ac.uk

The presence of shell-core structures in some extruded pellets is a well-known phenomenon [1], but it is very difficult to quantify the thickness of the external layer and its impact on mass trans- port kinetics. We present a methodology to characterize mass transport in extruded pellets that shows for the first time the ability to distinguish uniform structures from shell-core structures. The measurements are carried out with the zero length column (ZLC) technique [2] including both full equilibration and partial loading experiments [3]. Two commercial extruded materials from UOP, a Honeywell company, and UTSA-16 extrudates from SINTEF were used in this study. The two zeolite materials are shown to behave significantly differently when normal paraffins are used as the probe molecules. HISIV 3000 (silicalite) pellets show ZLC responses that are perfectly consistent with macropore diffusion control, while 5A pellets show a distinct "surface resistance" in addition to the internal diffusion process. The MOF pellets also show a distinct surface resistance, which can be detected using the ZLC and a suitable probe molecule.

The slower mass transport in the external shell is shown to be a macropore diffusion process by performing tests with different carrier gases. A detailed shell-core model is developed to analyze the responses in greater detail and determine the thickness of the external skin by the simultaneous regression of multiple experiments (different flowrates and partial loading runs) in the whole pellet and a fragment. This allows to determine quantitatively the thickness of the external layer, which is only a few microns thick.

The use of the ZLC provides a very efficient method to detect skin effects on pellets which are an important feature for quality control for manufactures. It also provides the ability to determine the effect of the skin resistance, allowing to estimate physical parameters that can be used to describe more accurately mass transport in adsorption and catalytic processes.

References:

1. Roberts CW. Molecular sieves for industrial separation and adsorption applications. In: Townsend RP, editor. The properties and applications of zeolites, London; The Chemical Society 1980 p. 103– 120.
2. Eic M. and Ruthven DM, A new experimental technique for measurement of intracrystalline difusivity. Zeolites 8 (1988) 40–45. https://doi.org/10.1016/S0144-2449(88)80028-9.
3. Brandani S. and Mangano E. The Zero Length Column Technique to Measure Adsorption Equilibrium and Kinetics: Lessons Learnt from 30 Years of Experience. Adsorption, 27 (2021) 319–351. https://doi.org/10.1007/s10450-020-00273-w

Deformation Dynamics of Nanoporous Solids upon Liquid Imbibition

Juan Sanchez[1]; Patrick Huber[2]

[1] Hamburg University of Technology

[2] Hamburg University of Technology and Deutsches Elektronen-Synchrotron DESY

Emails for correspondence: patrick.huber@tuhh.de, juan.sanchez@tuhh.de

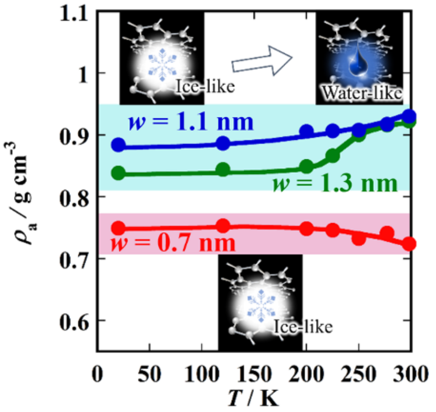
Capillarity-driven transport in nanoporous solids is ubiquitous in nature and is of increasing importance for the functionality of modern liquid-infused engineering materials. During imbibition, highly curved menisci are driven by negative Laplace pressures of several hundred atmospheres, exerting an enormous contractile load on an increasing portion of the porous matrix. Due to the challenge of simultaneously monitoring imbibition and deformation with high spatial resolution, the resulting coupling of solid elasticity to liquid capillarity has remained largely unexplored. Here, we study water imbibition in mesoporous silica using optical imaging, gravimetry, and high-resolution dilatometry. In contrast to an expected Laplace pressure-induced contraction, we find a square-root-of-time expansion and an additional abrupt length increase when the menisci reach the top surface. The final expansion is absent when we stop the imbibition front inside the porous medium in a dynamic imbibition-evaporation equilibrium, as is typical for water transport and transpiration in plants. These peculiar deformation behaviors are validated by single-nanopore molecular dynamics simulations and described by a continuum model that highlights the importance of expansive surface stresses at the pore walls (Bangham effect) and the buildup or release of contractile Laplace pressures as nanoscale menisci collectively advance, arrest, or disappear. Our model predicts that these observations are valid not only for water imbibition in silica, but for any imbibition process in nanopores, regardless of the liquid/solid combination. This also suggests that simple deformation measurements can be used to quantify surface stresses and Laplace pressures or transport in a wide variety of natural and artificial porous media.

Topological cluster structure of water confined in hydrophobic pores

Yasuhiro Sugiyama[1], Ryusuke Futamura[2] and Taku Iiyama[2,3]

[1] Graduate School of Medicine, Science and Technology, Shinshu University, 3-1-1 Asahi,
Matsumoto, Nagano, 390-8621 Japan
[2] Faculty of Science, Shinshu University, Japan
[3] Research Initiative for Supra-Materials, Shinshu University, Japan
Emails for correspondence: 23hs302c@shinshu-u.ac.jp, tiiyama@shinshu-u.ac.jp,
ryu_f@shinshu-u.ac.jp

The behavior of water confined in nanospaces is significantly different from that of bulk water. Water adsorption on activated carbon with hydrophobic surface shows a characteristic type V isotherm. Water fills the pores with strong intermolecular interactions and forms clusters inside the pores. We have been studied the adsorption mechanism from the experiments, X-ray diffraction (XRD) [1] and small-angle X-ray scattering (SAXS) [2]. The XRD gives direct information about the intermolecular structure of confined water. The confined water has an ice-like structure even at room temperature and exhibits a continuous solid-liquid phase transition phenomenon with temperature. The SAXS reveals the molecular assembly state, such as the size of the water clusters, and the differences in the shape and size of the clusters cause adsorption hysteresis.



Density changes of confined water in hydrophobic nanospaces

In this study, we show the anomalous temperature dependence of the water density confined in hydrophobic sub-nanometer spaces from in situ XRD measurements [3], and computational analysis, hybrid reverse Monte Carlo simulation (HRMC) and the persistent homology method. The persistent homology method provides geometric intermolecular structural information about disordered materials, such as amorphous and liquid materials. In sub-nanometer spaces, the density of confined water is very sparse compared to that of bulk ice even at room temperature, suggesting that the spatially distorted ice-like hydrogen bonding network would be formed in the nanospaces.

References:

1.T. Iiyama, K. Nishikawa, T. Otowa, K. Kaneko, J. Phys. Chem., 99, (1995) 10075.
2.T. Iiyama, Y. Kobayashi, K. Kaneko, S. Ozeki, Colloid and Surface A, 241, (2004) 207.
3.Y. Sugiyama, R. Futamura, T. Iiyama, Chem. Lett., 51, 760 (2022)

Acknowledgements:

This work was supported by JSPS KAKENHI (Grant Number 21K04977).

Quantitative Assessment of Hydrophilicity/Hydrophobicity in Nanoporous Materials

Carlos Cuadrado Collados,[a] Christoph Huber,[b] Jakob Söllner, a Jan-Paul Grass,[c] Alexandra Inayat,c Rustam Durdyyev,[d] Ana-Sunčana Smith,[d] Dorothea Wisser,[b] Martin Hartmann,[b] Matthias Thommes[a]*

[a] Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Institution of Separation Science and Technology Egerlandstr. 3, 91058 Erlangen, Germany

[b] Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen Center for Interface Research and Catalysis (ECRC), Egerlandstr. 3, 91058 Erlangen, Germany

[c] Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Institute of Chemical Reaction Engineering (CRT) Egerlandstr. 3, 91058 Erlangen, Germany

[d] PULS Group, Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute for Theoretical Physics, Centre for Computational Advanced Materials and Processes, IZNF, Cauerstraße 4, 91058 Erlangen, Germany

Email for correspondence: Matthias.Thommes@fau.de

We have developed a comprehensive strategy for assessing the surface chemistry of nanoporous materials by combining advanced adsorption studies, novel liquid intrusion techniques and solid-state NMR spectroscopy. The methodology was established on a well-defined system of model materials, the highly ordered mesoporous silica SBA-15, both pristine and functionalized with different amounts of trimethylsilyl (TMS) groups. The surface density of trimethylsilyl groups, was determined by quantitative 1H solid-state NMR spectroscopy under Magic Angle Spinning (MAS). 1H two-dimensional single quantum double quantum MAS NMR spectra reveal an intimate mixture of TMS and residual silanol groups on the surface. A full textural characterization of the materials was obtained by high-resolution argon at 87 K adsorption, coupled with the application of dedicated methods based on non-local-density functional theory. We further present a methodology to determine the effective contact angle of water adsorbed on the pore surfaces, which constitutes a powerful parameter for the characterization of the surface chemistry inside porous materials. The surface chemistry was found to vary from hydrophilic to a hydrophobic as the TMS functionalization content was increased, leading to contact angles from 0 ° (complete wetting) to 120 ° (non-wetting). For wetting and partial wetting surfaces, the contact angle was determined from the water sorption isotherms by applying the modified Kelvin equation on the desorption branch of the observed hysteresis loop, reflecting the thermodynamic liquid-vapour transition. On non-wetting surfaces, we investigated the pore filling of water by the application of a novel liquid water intrusion/extrusion experiment, applying the Washburn equation on the water intrusion branch which reflects the thermodynamic equilibrium vapor-liquid transition for a non-wetting fluid. Molecular simulations provide density profiles of water on pristine and TMS-grafted silica surfaces, which agree with the obtained experimental data.

The methodology presented here can in principle be used for assessing the hydrophilicity/hydrophobicity of a wide range of nanoporous materials for optimizing their properties towards applications in chromatographic separation or heterogeneous catalysis.

Investigating preferential adsorption of N2 from the air in Zeolite 13X using total neutron scattering

Marta Falkowska[1,2] and Daniel T. Bowron[2]

[1] Dept. of Chem. Eng., The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
[2] ISIS Neutron and Muon Source, Science and Technology Facilities Council, Harwell Campus, OX11 0QX, Didcot, UK
Email for correspondence: marta.falkowska@manchester.ac.uk

Medical oxygen concentrators (MOCs) utilise pressure swing adsorption to produce oxygen with ~88–92 vol% purity from ambient air. In this process a nitrogen-selective zeolite, most commonly molecular sieve 13X, is first used to adsorb nitrogen from an inlet stream of air at higher pressure (approx. 4 bar), and then subsequent adsorbent regeneration is achieved by passing the air through the sieve at lower pressure (below 1 bar).[1] By operating in fast adsorption-desorption cycles, the machines can produce a continuous stream of oxygen used in oxygen-therapies often prescribed for patients with deprived breathing capabilities.[2]

It has been suggested that the preferential adsorption of nitrogen from the air when compared to oxygen on the 13X molecular sieves is caused by the difference in the quadrupole moment of these two molecules, and the fact that for nitrogen it is three times higher than for oxygen.[3] Consequently, the affinity of nitrogen molecules to the electrostatic field of the zeolite is greater than for oxygen, and results in their enhanced adsorption from the air. Even higher adsorption of nitrogen can be achieved when the Na^+ ions present in the zeolite 13X framework are exchanged for Ca^{2+} or Li^+.[1,4]

To gain deeper insights, we conducted total neutron scattering experiments (TNS) to directly probe the molecular arrangement of adsorbates within zeolite 13X under varying pressure conditions. TNS has been proven to be an exceptional experimental tool for gaining insight into the local environment of liquids (e.g. water, benzene)[5,6] and gases (e.g. nitrogen, oxygen, methane) contained within pores of porous media such as MCM-41, and without making crystallographic assumptions.[7,8] Our research contributes to the molecular-level understanding of nitrogen adsorption from synthetic air in zeolite 13X (with Na^+ and Ca^{2+}), a critical step in the conscious design of gas-separating solutions. The focus on TNS provides a novel perspective on the behaviour of gases (N_2, O_2, CO_2 and N_2/O_2 mix) within zeolite 13X pores, offering valuable experimental insights for the enhancement of gas separation processes in healthcare applications.

References:

1. Ackley, Adsorption 2019, 25, 1437.
2. Pan *et al*., J. Nanomater. 2017, 7, 195.
3. Buckingham *et al*., JACS 1968, 90, 3104.
4. E.g. Wu *et al.*, Eg. Ind. Eng. Chem. Res. 2016, 55, 4676.; Richards et al., J. Porous Mat. 1995, 2, 43.
5. Mancinelli *et al*., J. Phys. Chem. B 2009, 113, 50, 16169.
6. Falkowska *et al*., Angewandte Chemie International Edition Engl., 2018, 57, 4565.
7. Soper *et al*., Chem. Phys. Lett. 2017, 683, 529.
8. Soper *et al*., J. Chem. Phys. 2021, 154, 184503.

Acknowledgements:

The authors would like to thank Gemma Draper and Mark Kibble for their help in preparing the experimental setup at ISIS. The authors would also like to acknowledge the ISIS neutron and muon source for awarding the beam time RB2200307.

Selectivity in adsorption of responsive metal-organic frameworks

Irena Senkovska[1], Volodymyr Bon[1], Leila Abylgazina[1], Mariia Maliuta[1], and Stefan Kaskel[1]

[1]Inorganic Chemistry I, Dresden University of Technology, Bergstr. 66, 01069 Dresden, Germany
Emails for correspondence: irena.senkovska@tu-dresden.de, volodymyr.bon@tu-dresden.de

Flexible metal-organic frameworks (MOFs) that show reversible guest-induced phase transitions between closed and open pore phases have enormous potential for highly selective, energy-efficient separations, because they can selectively respond to external stimuli, adapting their pore size triggered by adsorption-induced gating or breathing.

The flexible framework DUT-8 is the focus of the present contribution. It consists of paddle wheels, 2,6-naphthalenedicarboxylate linkers, and 1,4-diazabicyclo(2.2.2)octane pillars forming a primitive cubic net. The composition of the metal node, crystal size, morphology, and conformation are used to effectively tune the responsivity of DUT-8.

The *macrosized crystals* of DUT-8 show selective guest responsivity associated with a pronounced cell volume change (~250%) upon gate opening. For DUT-8(Ni), an adsorption-induced transition from a closed-pore (cp) to an open-pore (op) phase can be triggered by nitrogen, carbon dioxide, or hydrocarbons at their standard boiling points, as well as by the majority of solvent vapors and CO_2 at high pressure at room temperature. *Nanocrystals* of DUT-8 are rigid instead and show reversible uptake of gasses after desolvation. This is a behavior typical for conventional microporous solids.

The mechanism behind gate opening relies on the hinge energetics of the network nodes, balancing strain energy (favoring the open form) and linker-linker interactions (stabilizing the closed form). The guest molecules' interactions with the pore interior counteract these linker-linker interactions and induce gate opening. For gas separation, selective pore opening can induce colossal selectivity, which is a crucial aspect of energy-efficient separation processes.

DUT-8(Ni) is able to discriminate between CO_2 and CH_4 in the mixture of these gases at room temperature.[1] It is also able to isotopolog-selective switching, demonstrating D_2 over H_2 selective responsivity.[2]

The *macrocrystals* of DUT-8(Zn) show selective reopening in the presence of dichloromethane (DCM) over alcohols, wherever the crystal downsizing to *micron size* unexpectedly reverses the gate opening selectivity, causing DUT-8(Zn) to open its nanosized pores for alcohols but suppressing the responsivity towards DCM.[3]

References:

1. M. Sin, N. Kavoosi, M. Rauche, J. Pallmann, S. Paasch, I. Senkovska, S. Kaskel, E. Brunner, *Langmuir* 2019, 35, 3162.
2. L. Bondorf, J. L. Fiorio, V. Bon, L. D. Zhang, M. Maliuta, S. Ehrling, I. Senkovska, J. D. Evans, J. O. Joswig, S. Kaskel, T. Heine, M. Hirscher, *Sci. Adv*. 2022, 8, eabn7035.
3. L. Abylgazina, I. Senkovska, R. Engemann, N. Bönisch, T.E. Gorelik, Ch. Bachetzky, U. Kaiser, E. Brunner, and S.Kaskel, *under revision*.

Acknowledgements:

The authors gratefully acknowledge the financial support from DFG (Deutsche Forschungsgemeinschaft) under contracts FOR 2433.

Insights into Capillary Condensation and Hysteresis in Nanoporous Materials from New Simulation Methods

Randall Q. Snurr[1], Zhao Li[1], Filip Formalik[1], Jesse Prelesnik[2], and J. Ilja Siepmann[2]

[1] Department of Chemical & Biological Engineering, Northwestern University, Evanston, IL 60208, USA
[2] Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA
Email for correspondence: snurr@northwestern.edu

Capillary condensation and the related phenomenon of adsorption hysteresis can impact applications of porous materials such as gas storage, separations, and adsorption cooling. To better understand these phenomena, we have calculated the adsorption isotherms for methane, ethane, propane, and n-hexane from atomistic grand canonical Monte Carlo (GCMC) simulations in a metal-organic framework having both micropores and mesopores [1]. At low temperatures, the calculated isotherms exhibit sharp steps accompanied by hysteresis. As a complementary simulation method, canonical (NVT) ensemble simulations with Widom test particle insertions are demonstrated to provide additional information about these systems. The NVT+Widom simulations provide the full van der Waals loop associated with the sharp steps and hysteresis, including the locations of the spinodal points and points within the metastable and unstable regions that are inaccessible to GCMC simulations. The simulations provide molecular-level insight into pore filling and equilibria between high- and low-density states within individual pores. The effect of framework flexibility on adsorption hysteresis was also investigated for methane in IRMOF-1 [1].

We have also the adsorption and desorption isotherms for argon at 87 K in 1873 MOFs from the CoRE MOF database [2] and for short *n*-alkanes in selected MOFs. Analysis of the molecular configurations showed at least two different mechanisms and origins of hysteresis: one involving a transition in the pores similar to a liquid-to-solid transition and one more similar to a gas-to-liquid transition. The validity of an empirical relationship for the critical pore diameter for hysteresis was also tested using the calculated argon desorption isotherms. The simulations reveal some structures where isotherms exhibit two steps in the adsorption branch and only one step in the desorption branch. Hysteresis loops with a different number of adsorption and desorption steps are quite rare in the literature. To better understand why hysteresis is observed in the GCMC simulations, the concept of the transition probability, which describes the probability of observing a step in the adsorption isotherm at a given pressure in a GCMC simulation, is introduced. We used three different methods to calculate the transition probabilities, and we validated that the three methods yielded similar results. The transition probability can be used as a method to quantify and test the convergence of GCMC simulations in the metastable region of an adsorption process.

References:

1. Z. Li, J. Turner, R.Q. Snurr, Computational investigation of hysteresis and phase equilibria of n-alkanes in a metal-organic framework with both micropores and mesopores," *Comms. Chemistry*, 6 (2023) 90.
2. Y.G. Chung, E. Haldoupis, B.J. Bucior, M. Haranczyk, S. Lee, H. Zhang, K.D. Vogiatzis, M. Milisavljevic, S. Ling, J.S. Camp, B. Slater, J.I. Siepmann, D.S. Sholl, R.Q. Snurr, Advances, updates, and analytics for the computation-ready, experimental metal-organic framework database: CoRE MOF 2019, *J. Chem. Eng. Data*, 64 (2019) 5985–5998.

Acknowledgements:

This work was supported by the U.S. Department of Energy, Office of Basic EnergyvSciences, Division of Chemical Sciences, Geosciences and Biosciences under Award No. DE-SC0023454.

Anomalous interaction between propylene and Ag cation in zeolites

Hideki Tanaka,[1,*] Tomoki Ogata,[2] Motomu Sakai,[3] Masahiko Matsukata,[4] Katsuya Teshima[1,2]

[1] Research Initiative for Supra-Materials (RISM), Shinshu University, Japan
[2] Department of Materials Chemistry, Faculty of Engineering, Shinshu University, Japan
[3]Research Organization for Nano & Life Innovation, Waseda University, Japan
[4]Department of Applied Chemistry and Advanced Research Institute for Science and Engineering, Waseda University, Japan
Email for correspondence: htanaka@shinshu-u.ac.jp

Recently, Ag-exchanged zeolite X (Ag-X) membrane was found to be promising for propylene/propane separation [1]; however, the separation mechanism providing the high C_3H_6 selectivity is still unclear. To elucidate this mechanism, it is essential to identify the positions of the Ag cations in the zeolite X framework, and to clarify the adsorption behavior of C_3H_6 on Ag-X by molecular modeling. In this study, in situ synchrotron X-ray powder diffraction of Ag-X was measured, and the positions of Ag cations were identified by the Rietveld and MEM analyses, and then the obtained structure was used to understand the adsorption mechanism of C_3H_6 by ab initio molecular dynamics (MD) simulation.

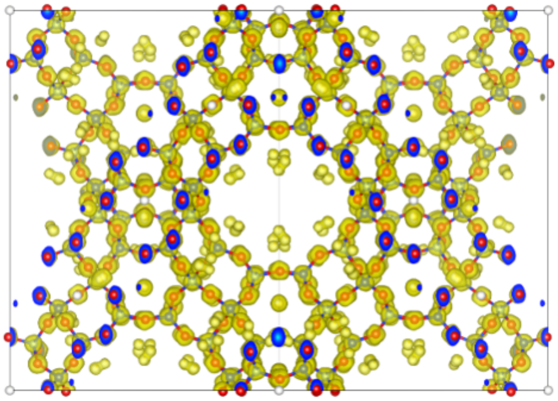


Fig. 1 Structure of Ag-X obtained from the Rietveld and MEM analyses.

In situ XRPD measurements were carried out at SPring-8 (BL02B2). The Rietveld analysis (RIETAN-FP) of the obtained XRPD pattern was successfully performed (Rwp = 7.7, S = 1.5) (Fig. 1), and the fractional coordinates (I–VI sites) and occupancies of Ag cations were identified. In addition, the electron distribution of the Ag cation was observed at each site by the MEM analysis (Dysnomia) (Fig. 1), which shows the validity of the Rietveld analysis. The only Ag cation sites that should contribute to C_3H_6 adsorption are the IV, V, and VI sites. The ratio of Ag cations in these sites to total Ag cations was 0.53. On the other hand, the number of adsorbed C_3H_6 molecules per Ag cation was estimated to be ca. 0.55 from the low relative pressure region of the C_3H_6 adsorption isotherm (313 K). In other words, if we assume that one C_3H_6 molecule is adsorbed per Ag cation, the ratio of Ag cations that can contribute to C_3H_6 adsorption is 0.55, which is in good agreement with the result from the Rietveld analysis.

Ab initio MD simulation based on the Ag-X structure from the Rietveld method showed that the 12-membered ring channels of Ag-X were blocked by the adsorbed C_3H_6 molecules on Ag cations and the C_3H_6 molecules diffused by hopping between the Ag cations. This blocking should prevent the diffusion of propane inside Ag-X, which does not have a specific interaction with the Ag cation and contribute to the high C_3H_6 selectivity of the Ag-X membrane. The most interesting finding revealed by this ab initio MD simulation is that the Ag cations exhibit extremely specific motion, resembling the role of a “pump” that releases and diffuses the adsorbed C_3H_6.

References:

1. M. Sakai et al., ACS Appl. Mater. interfaces 12 (2020) 24086–24092; 11 (2019) 4145–4151.

Unusual coexisting adsorption and structural transformations mechanism in Nano-Porous Materials

Bogdan Kuchta[1,2], Bartosz Mazur[1], Lucyna Firlej[1,3], 1,3Malgorzata Stankiewicz[1,3]

[1]Department of Micro, Nano, and Bioprocess Engineering, Faculty of Chemistry, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland

[2] MADIREL, CNRS, Aix-Marseille University, 13397 Marseille, France

[3]Laboratoire Charles Coulomb, University of Montpellier-CNRS, 34095 Montpellier, France
Email for correspondence: Bogdan.kuchta@pwr.edu.pl

The phase behavior of confined fluids adsorbed in nanopores differs significantly from their bulk counterparts and depends on the chemical and structural properties of the confining structures. In general, phase transitions in nanoconfined fluids are reflected in stepwise adsorption isotherms with a pronounced hysteresis. Here, we show experimental evidence and an in-silico interpretation of the reversible stepwise adsorption isotherm which is observed when methane is adsorbed in the rigid, crystalline metal−organic framework IRMOF-1 (MOF-5) [1]. In a very narrow range of pressures, the adsorbed fluid undergoes a structural and highly cooperative reconstruction and transition between low-density and high-density nanophases, as a result of the competition between the fluid−framework and fluid−fluid interactions. This mechanism evolves with temperature: below 110 K, a reversible stepwise isotherm is observed, which is a result of the bimodal distribution of the coexisting nanophases. This temperature may be considered as a critical temperature of methane confined to nanopores of IRMOF-1. Above 110 K, as the entropy contribution increases, the isotherm shape transforms to a common continuous S-shaped form [2] that is characteristic to a gradual densification of the adsorbed phase as the pressure increases. The other IRMOF structures have been also modeled and the results compared to the IRMOF-1 case. The density distribution shows symmetric structures which structural properties evolve in a function of uptake and temperature [3].

References:

1. B. Mazur, F. Formalik, K. Roztocki, V. Bon, S. Kaskel, Alexander V. Neimark, Lucyna Firlej, and Bogdan Kuchta, Quasicontinuous Cooperative Adsorption Mechanism in Crystalline Nanoporous Materials, J. Phys. Chem. Lett. 2022, 13, 6961−6965

2. D. Fairen-Jimenez, N. A. Seaton, T. Düren, Unusual Adsorption Behavior on Metal-Organic Frameworks. Langmuir 2010, 26 (18), 14694−14699.

3. Kuchta, B.; Dundar, E.; Formalik, F.; Llewellyn, P. L.; Firlej, L. Adsorption-Induced Structural Phase Transformation in Nanopores. Angewandte Chemie - International Edition 2017, 56 (51), 16243−16246.

Acknowledgements:

Supported by the National Science Centre (NCN), Poland (grant: 2022/45/B/ST8/02028).

Understanding the Origins of Reversible and Hysteretic Pathways of Adsorption Phase Transitions by Mesocanonical Ensemble Monte Carlo Simulations

Shivam Parashar[1], Alexander Neimark [1]

[1] Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey,
Piscataway, New Jersey 08854, United States

Emails for correspondence: sp1709@soe.rutgers.edu, aneimark@rutgers.edu

Phase transformations in adsorbed fluids frequently involve metastable states and hysteretic transitions. This phase behavior is revealed in adsorption experiments with mesoporous materials and most prominently in Grand Canonical Monte Carlo (GCMC) simulations, which are most commonly used to calculate adsorption isotherms. GCMC simulation typically produces a hysteretic adsorption-desorption isotherm with stepwise transitions. Due to the difference in experimental and simulation conditions (range of fluctuations and time of observation), the positions of experimentally observed and simulated transitions may differ significantly. Also, the hysteretic GCMC isotherm does not allow for determination of the position of true equilibrium between the coexisting phases. Alternative methods, such as the canonical ensemble, address this limitation fixing the number of particles and measuring the chemical potential using the Widom insertion method. Canonical ensemble generates a Van der Waals type isotherm that traces stable, metastable, and unstable states. However, calculation of chemical potential is computationally expensive, especially at higher fluid densities, due to a difficulty of inserting probe particles.

Mesocanonical ensemble 1, 2, 3 provides an efficient method of MC simulations (MCEMC), called the gauge cell method, for calculating the chemical potential, sampling of metastable and labile states and producing a continuous Van der Waals type phase diagram of nanoconfined fluids. This method involves coupling the sample cell with a finite volume reservoir (gauge cell), which restricts the density fluctuations and stabilizes the adsorbed phase. The MCEMC method allows for calculating the positions of true phase equilibrium and the nucleation barriers, which control the hysteretic phase transitions. In this work, we implemented the MCEMC method in the open source software RASPA and demonstrated its capabilities and efficiency for studies adsorption on practical MOFs, like IRMOF-1, ZIF-412, UiO-66, Cu-BTC, IRMOF-74-V, VII, and IX. The calculated adsorption isotherms are tested against the experiments and compared with the results of grand canonical, transition matrix, canonical ensemble MC simulations.

References:

1. Neimark, A. V.; Vishnyakov, A., Gauge cell method for simulation studies of phase transitions in confined systems. Physical Review E 2000, 62 (4), 4611-4622.
2. Vishnyakov, A.; Neimark, A. V., Studies of Liquid−Vapor Equilibria, Criticality, and Spinodal Transitions in Nanopores by the Gauge Cell Monte Carlo Simulation Method. The Journal of Physical Chemistry B 2001, 105 (29), 7009-7020.
3. A.V. Neimark and A. Vishnyakov, - A Simulation Method for the Calculation of Chemical Potentials in Small, Inhomogeneous, and Dense Systems, Journal of Chemical Physics, 2005, V. 122, 234108.

Acknolegments: This work is supported by the NSF CBET grant 1834339.

Flat-histogram Simulations of Water in MOFs: Advanced Strategies for Overcoming Sampling Challenges

Daniel W. Siderius[1], Harold W. Hatch[1], and Vincent K. Shen[1]

[1] Chemical Sciences Division, National Institute of Standards and Technology, 100 Bureau Dr,
Gaithersburg, MD, 20899, USA
Email for correspondence: daniel.siderius@nist.gov

Adsorption of water by porous materials has recently reemerged as an area of interest due to its possible application as a platform for harvesting water from humid air. Combined with the widespread application of computational screening of adsorbent materials for various applications, molecular simulations of water in confinement are once again an area of ongoing investigation. However, the key challenge of water simulations in porous materials remains unchanged: due to strong water-water hydrogen bonding, adsorption of water occurs primarily at high relative humidity or low temperature and typically over a narrow pressure range [1], akin to Type V isotherms in the standard IUPAC classification scheme. Hydrogen bonding networks also encourage coalescence of water in pores rather than monolayer formation [2,3]. These challenges are exacerbated in hydrophobic metal-organic frameworks (MOFs) with cage-like pores, where adsorption occurs non-sequentially, but via abrupt steps in which one cage (cavity) fills with a single cluster of water in each step [1]. These simulation challenges are manifested by slow equilibration, inefficient sampling, and large uncertainties in ensemble averages [1]. The introduction of so-called superhydrophobic materials only amplifies these simulation challenges. Recent work has explored strategies to overcome the sampling challenges by using energy look-up tables, insertion (deletion) biases, and continuous-fractional component Monte Carlo [1].

We approach the problematic sampling of water adsorption in hydrophobic materials through a similar suite of simulation tools, starting with flat-histogram Monte Carlo (MC) and adding advanced MC moves, and then parallel simulations, all focuses on improving the efficiency with which the statistical phase space is sampled. In particular, we introduce configurational-bias MC operations that are tuned for adsorption in crystalline materials and specialized MC moves that address the proclivity of water to form clusters. We implement flat-histogram MC using Wang-Landau and Transition-matrix biases, which additionally allows us to examine water cluster formation via the macrostate probability distribution, such as through identification of free-energy barriers between individual clusters. However, the water-clustering effect necessitates the introduction of new analysis tools for converting the macrostate probability distribution to ensemble averages including the adsorption isotherm. These advanced strategies are implemented using the FEASST Monte Carlo toolkit [4], which provides modularity and is accessible to other researchers. The end effect is to both present simulation results for specific materials that highlight the challenges of water adsorption and use these prototype systems to suggest specific strategies for other researchers that simulate water adsorption.

References:

1. Zhang and Snurr, J Chem Phys C, 121:24000 (2017);
2. Striolo, Gubbins, Chialvo, and Cummings, Mol Phys 102:243 (2004);
3. Sarkisov, Centineo, and Brandani, Carbon 118:127 (2017);
4. Hatch, Mahynski, and Shen, J Res NIST, 123:123004 (2018).

Mechanism of Vapor Sorption and Sorption-Induced Deformation in Bacterial Spores

Gennady Y. Gor[1,2], George W. Scherer[3], Howard A. Stone[1]

[1] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA
[2] Dept. of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, NJ, USA
[3] Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ, USA
Email for correspondence: ggor@princeton.edu

Bacterial spores have outstanding properties from the materials science perspective, which allow them to survive extreme environmental conditions. Recent work by Harrellson et al. [1] studied the mechanical properties of *Bacillus Subtilis* spores, and unique evolution of these properties with the change of humidity. The experimental measurements were interpreted assuming that the spores behave as water-filled porous solids, subjected to hydration forces. Here we revisit their experimental data using literature data on vapor sorption on spores and ideas from polymer physics. We demonstrate that upon the change of humidity the spores behave like hydrogels with respect to their swelling, elasticity, and relaxation times. This picture is consistent with the knowledge of the materials comprising the bacterial cell walls – cross-linked peptidoglycan. Our results provide an interpretation of the mechanics of bacterial spores and can help in developing novel synthetic materials mimicking the mechanical properties of the spores.

References:

1. Harrellson, S.G., DeLay, M.S., Chen, X., Cavusoglu, A.H., Dworkin, J., Stone, H.A. and Sahin, O., Hydration solids, Nature, 619, (2023) 500-505.

Acknowledgements:

G.Y.G. thanks NSF CBET-1944495 grant for the support.

CPM9 | REPORT OF ABSTRACTS

TUESDAY, MAY 21, 2024

Combining multiple functions to achieve process intensification in adsorptive separations

Mohsen Gholami[1]; Ravi Sharma[1]; Matthias Schoukens[1]; Gille Wittewrongel[1]; Rahul Maity[1]; Joeri Denayer[1]

[1] Dept. of Chem. Eng., Vrije Universiteit Brussels, BE

Email for correspondence: joeri.denayer@vub.be

There is a tendency in chemical industry to electrify thermal chemical processes in order to reduce carbon footprint 1. Therefore, electrification of Thermal Swing Adsorption processes is also of interest. Alternative heating methods such as Joule heating (Electrical Swing Adsorption - ESA) [2], Microwave heating (Microwave Swing Adsorption - MSA) [3] and Magnetic Induction heating (Magnetic Induction Swing adsorption –MISA) [4] have been considered by various researchers to heat and regenerate the adsorbent bed. These methods have a number of advantages, such as the direct, contactless and localized heating of the bed, resulting in reduced heat losses; high heating rates and an on/off behavior, offering perspectives for improved process control and reduced cycle time. Nevertheless, these electrified regeneration methods require materials that are compatible with the respective heating method. Joule heating requires an electrically conductive path, microwave heating requires dielectric properties for the adsorbent material and induction heating requires an adsorbent with magnetic properties. Obviously, common porous solids don't have all of these properties. Therefore, composite materials have to be developed such that the resulting hybrid adsorbent becomes susceptible to the applied heating method. Such materials can be shaped as beads, extrudates, 3D-printed materials or monoliths. This does not only affect the separation performance, but also the heating behavior.

In this paper, a number of approaches to prepare hybrid materials for electrified Temperature Swing Adsorption processes will be discussed, from literature and our own work. Examples in the field of carbon capture, direct air capture and solvent recovery will be given.

References:

1. M. Bonheure, L. Vandewalle, G. Marin and K. Van Geem, Dream or reality? Electrification of the chemical process industries, Chemical Engineering Progress, 117(3). (2021) 37-42.
2. R.P.P.L. Ribeiro, C.A. Grande, A.E. Rodrigues, Electric Swing Adsorption for Gas Separation and Purification: A Review, Sep. Sci. Technol. 49 (2014) 1985–2002.
3. Reuß, J., Bathen, D., & Schmidt-Traub, H. (2002). Desorption by microwaves: Mechanisms of multicomponent mixtures. Chemical Engineering and Technology, 25(4), 381–384. https://doi.org/10.1002/1521-4125(200204)25:4<381::AID-CEAT381>3.0.CO;2-0
4. Gholami, M., Verougstraete, B., Vanoudenhoven, R., Baron, G. V., Van Assche, T., & Denayer, J. F. M. (2021). Induction heating as an alternative electrified heating method for carbon capture process. Chemical Engineering Journal, 431.

Acknowledgements:

The authors would like to acknowledge VLAIO for the financial support (HBC.2019.0109).

Measurement of multicomponent adsorption isotherms based on a temperature-step approach and mass spectrometry

Nicolas Chanut[1], Robbe Van Loenhout[1], Cesar Parra Cabrera[1], Masaya Sugihara[1], João Fernandes[1], Margot Verstreken[1], Leen Boullart[1], Rob Ameloot[1]

[1] Center for Membrane Separations, Adsorption, Catalysis, and Spectroscopy (cMACS), KU Leuven,
Celestijnenlaan 200F, 3001 Leuven, Belgium
Email for correspondence: nicolas.chanut@kuleuven.be

Equilibrium single-component measurements are routinely performed using volumetric or gravimetric techniques. However, because industrial processes deal with mixtures and different molecules compete for the same adsorption sites, single-component isotherms are of limited use in designing a separation process. Researchers have long tried to predict mixture adsorption based on single-component isotherms (e.g., ideal adsorbed solution theory), but non-ideal behavior remains challenging to forecast without actual mixture adsorption experiments. Unfortunately, measuring multicomponent adsorption is complex and time consuming. A range of methods has been developed, yet none combines ease of operation, straightforward data analysis, and fast measurements. Breakthrough methods, by far the most common approach, illustrate this trade off. While it provides robust multicomponent adsorption data, each data point requires a few hours to one day due to the relatively large adsorbent mass (> 100 mg) and the reactivation of the adsorbent between each measurement, making this approach time-consuming for the collection of full multicomponent isotherms.

In this presentation, we will present a new methodology for the rapid measurement of reliable multicomponent adsorption isotherms. Instead of a concentration change in the atmosphere surrounding the adsorbent, a sudden temperature change of the adsorbent is used to induce full desorption after equilibration at every partial pressure. The desorbed fraction is quantified downstream using a mass spectrometer, by integration of the signal in excess of its baseline. Because of the use of downstream MS analysis, the method can be readily extended to multicomponent measurements (Figure 1).

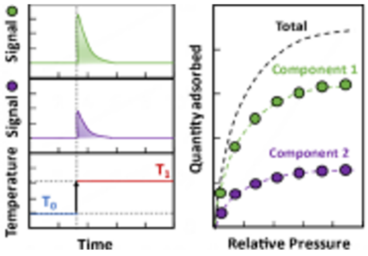


Figure 1: Multicomponent isotherm measurement approach. A heat pulse is applied to desorb all guest molecules, which are quantified using MS. Each desorption pulse yields one point on the multicomponent isotherm, i.e., one uptake value for each component for a given mixture composition.

Compared to breakthrough measurements the temperature-step approach is much faster. The temperature-step approach uses much smaller adsorbent quantities (< 100 µg), which considerably decreases the equilibration time. Moreover, since at each step all guest molecules are thermally desorbed, no separate re-activation step of the adsorbent is necessary in between measurements. Our results show a data acquisition time of < 10 min per point on a multicomponent isotherm and straightforward data analysis (*i.e.*, integration of the MS signal).

The methodology has first been validated for the measurement of single-component isotherms. The high sensitivity of a triple-quadrupole MS allows for the quantification of small amounts of pre adsorbed species (*e.g.*, 1 nmol or 60 ng for 1-propanol). A full isotherm of 1-propanol on ZIF-8 (using a 57µg sample) was compared to results obtained by Quartz Crystal Microbalance and volumetry measurements, showing a good agreement between the different methods. Results of multicomponent adsorption measurements on industrially relevant adsorbents and their interpretation will be further detailed in the presentation.

Direct visualization of Al distribution inside zeolite crystals

Yoshihiro Kamimura[1], Tetsuya Kodaira[1] and Akira Endo[1]

[1] National Institute of Adavance Industrial Science and Technology (AIST), Central 5,
1-1-1 Higashi,Tsukuba, Ibaraki 305-8565, Japan
Email for correspondence: endo-akira@aist.go.jp

Zeolites are porous material widely used as a catalyst, adsorbent in many industrial fields. Zeolite framework consist of mainly Si, Al and O, and it is important to control the position of Al at the atomic level. In addition, the size of zeolite particles are generally micron order, and the distribution of elements at that scale is expected to significantly affect the properties of zeolites. In this study, we aim to characterize zeolites in more detail by combining the visualization of atomic distribution at sub-micron scale by scanning electron microscopy and the evaluation of zeolite pore structure by a gas adsorption method. SEM is widely used as a tool to observe surfaces and microscopic shapes and sizes. Retarding methods have made it possible to observe the topmost surface structure of a sample with a resolution of about 1 nm using low acceleration voltages less than 1kV [1]. In addition, it has become possible to obtain information on the internal structure of particles by forming a smooth cross-section using Ar ions [2], and to directly observe the compositional distribution inside the sample by combining this technique with the EDS method. In this study, visualization of aluminum distribution inside the zeolites was performed by applying high-resolution FE-SEM and EDS mapping. Commercially available and synthesized zeolites with various Si/Al were selected as target material and Al-distribution inside zeolite particles were visualized. As shown in Figure 1, the Al distribution inside the zeolite particle is clearly observed. Furthermore, high-resolution Ar physisorption measurements were conducted to correlate with the detailed pore textural assessment. The origin of this Al-distribution will be discussed in the presentation.

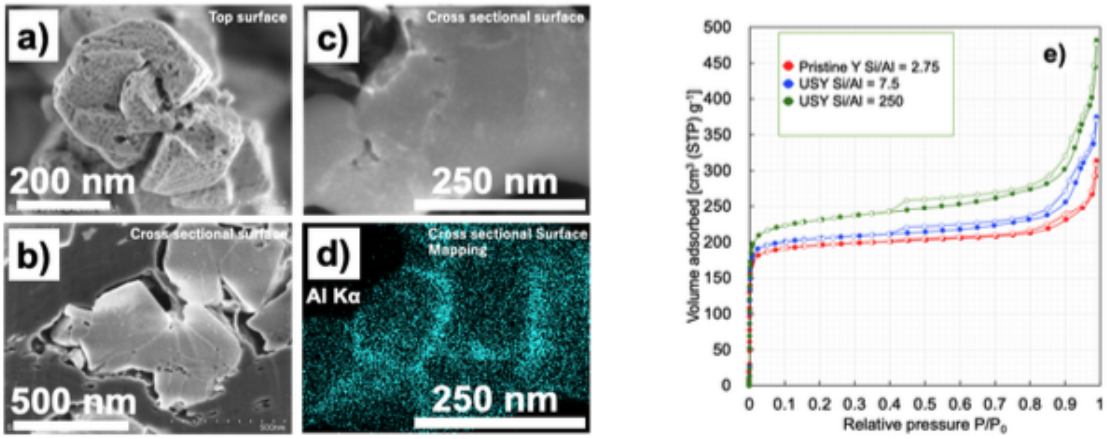


Figure 1. (a) Top-surface and (b) cross-sectional surface FE-SEM images for protonated-form pristine zeolite Y (Si/Al = 2.75). Cross-sectional surface (c) FE-SEM and (d) EDS mapping images for same zeolite Y sample at different viewing position. (e) Argon physisorption isotherms at 87.3K.

References:

1. A.Endo, M. Yamada, S. Kataoka, T. Sano, Y. Inagi, A. Miyaki, Direct observation of surface structure of mesoporous silica with low acceleration voltage FE-SEM. Colloids Surf. A Physicochem. Eng. Asp. 2010, 357, 11–16.

Acknowledgements:

Moonshot Project entitled as the "Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society" from the New Energy and Industrial Technology Development Organization (NEDO) funding agency, Japan.

Predicting the pore-structure transport relationship in disordered alumina using hyperpolarized xenon MRI and NMR cryodiffusometry

S. M. Collins[1,2], H. Williams[2], G. E. Pavlovskaya[2], T. Meersmann[2], A. Harrison[2], C. Vallée[1], T. Chevalier[1], D. Lofficial[1] and S. P. Rigby[2]

[1] IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
[2] University of Nottingham, Nottingham, United Kingdom
Email for correspondence: enysmc@nottingham.ac.uk

The characterization of porous aluminas has been a long-standing problem due to their complex, disordered porous structures, with structural features ranging from the nanometre to the millimetre scale. There is a need to understand how the pore structure influences mass transport, to guide new catalyst designs and optimize catalytic processes. However, the complex, hierarchical nature of pellet structure often means that a so-called "brute force" approach is beyond the reach of current computing power, and methods enabling selection of the key structural features to incorporate into a model are necessary. In this work, the combination of hyperpolarized (hp) ^{129}Xe MRI and NMR cryodiffusometry, has been used to probe the structural-transport relationship of bimodal amorphous gamma alumina support pellets, with different degrees of controlled macroporosity to assess the key void space features determining tortuosity.

NMR cryodiffusometry experiments, using water or cyclohexane as the probe fluid, were performed using both boundary and scanning, and both melting and freezing curves. These experiments were coupled with complementary DSC thermoporometry to corroborate the cryoporometry results, and FIB-SEM experiments to aid the interpretation of the NMR data. A novel hp ^{129}Xe NMR/I technique has been developed to allow the probing of the spatial distribution of rates of gas uptake across individual catalyst pellets, and this to be related to pore structure and, also, catalytic performance.

The self-diffusivity of water as a function of molten fraction has been measured using NMR cryodiffusometry[1], and, thence, the relative importance of different aspects of the void space, and various bins within the pore size distribution, to mass transport rates has been investigated. Pore structure models have been fitted to the tortuosity versus molten fraction plots, to infer the basic geometrical character. Hp ^{129}Xe MRI allows for the study of low-density, gas-phase mass-transport, such that diffusion can be measured in the Knudsen diffusional regime, instead of the purely molecular regime, more closely mimicking the transport processes that would occur in gas-phase catalytic reactions[2]. Whilst NMR cryodiffusometry measures the average self-diffusion coefficient of liquid water over 10s of microns, the hp xenon experiments measures the impact of long-scale structural features on pellet mass transfer. Through the combination of these two techniques, structural and diffusional heterogeneities at different length scales can be measured, and their overall contribution to the observed catalytic activity evaluated.

References:

1. E. Perkins *et al.*, Determination of the percolation properties and pore connectivity for mesoporous solids using NMR cryodiffusometry, Chemical Engineering Science, 63 (2008) 1929–1940
2. G. Pavlovskaya *et al.*, NMR Imaging of Low Pressure, Gas-Phase Transport in Packed Beds Using Hyperpolarized Xenon-129 AIChE, 61 (2015), 4013–4019

Acknowledgements:

I would like to thank IFP Energies nouvelles for sponsoring this research.

Kinetic measurements on monoliths using the Adsorption Differential Volumetric Apparatus (ADVA)

Riccardo Rea[1], Mohsen Gholami[2], Joeri Denayer [2], Stefano Brandani[1], Enzo Mangano[1]

[1] University of Edinburgh, Edinburgh, United Kingdom
[2] Vrije Universiteit Brussels, Brussels, Belgium
Email for correspondence: E.Mangano@ed.ac.uk

In recent years, the ever increasing development of manufacturing techniques has allowed the synthesis of a wide range of structured adsorbents designed to address some of the shortcomings of conventional pelletised materials. Channel shapes and flow patterns are engineered to minimise pressure drop, improve adsorption/desorption kinetics and maximise accessibility to the active material. The main challenges in the field of monoliths are commonly associated with the synthesis and production process while it is often neglected that testing and characterise these structured materials is equally challenging. Monoliths are produced in a variety of shapes and sizes and this prevents the use of most conventional and commercial adsorption techniques. Most of these systems (microbalances and commercial volumetric apparatuses, for example) are generally designed to minimise dead volumes, sample units normally house relatively small quantities of powders or pelletised materials and accessibility to the uptake cells is often very limited. This means that in many cases monoliths need to be broken down to smaller pieces or fragments to be tested in the most common apparatuses, providing only partial insights on the performance of the formed material.

The Adsorption Differential Volumetric Apparatus (ADVA) is a novel volumetric system designed with two symmetric branches (sample and reference) and relies on a differential pressure transducer across the sample and reference side for increased accuracy. This allows the system to provide highly accurate equilibrium and kinetic measurements in the entire pressure range using very small sample masses (<100 mg). The system has a modular design that allows to adapt the uptake cell to samples of different sizes and shapes, making it ideal for the characterization of structured adsorbents.

In this work, we present gas transport measurements of CO_2 and N_2 at different pressure levels on a number of monoliths. Samples include zeolite-based adsorbents with different pores sizes extruded as monoliths of different wall sizes manufactured at Vrije Universiteit Brussels.

The measurements provide insights on the process performance of the material as well as the manufacturing process.

References:

1. J. Wang, E. Mangano, S. Brandani, F. Brandani, P. Pullumbi, A novel adsorption differential volumetric apparatus to measure mass transfer in nanoporous materials, Separation and Purification Technology, Volume 283, 2022.

Towards “infinite”selectivities in CO2/CH4 and CO2/N2 separations with MgNa-GIS flexible zeolite

J. Al Atrach, Y. Xiong[1], E. B. Clatworthy[1], V. Valtchev[1,*] and R. Guillet-Nicolas[1,*]

[1] Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France.

Email for correspondence: remy.guillet@ensicaen.fr

Thanks to their perfectly tailored framework topologies, small-pore zeolites have received much attention in the last years for separation of small gases with high added values.[1]. However, finding the best zeolites for such task is not easy since many parameters have to be synergistically screened. In this context, we present a comprehensive study mixing DFT calculations and molecular dynamics simulations to isolate the best formulations for CO_2 separation. This first step led to the template-free synthesis of stable Na-GIS followed by partially ion-exchange with Mg^{2+} cations. The parent Na-GIS and partially-exchanged NaMg-GISs were thoroughly characterized using state-of-the-art techniques, and studied for their applicability for CO_2 adsorption and $CO_2/N_2/CH_4$ separation through single component adsorption at both low and high pressures and dynamic breakthrough curve analysis methods. In all cases, deep investigations were conducted using advanced and high-precision sorptiometry to understand the effect of the network dimensionality, flexibility and accessibility on the resulting adsorption behaviour and heat of adsorption values with pure component and gas mixtures. Finally, simplified fast cycling experiments consisting of five complete dynamic cycles were conducted to evaluate the potential of this material in pseudo realistic flow setups. Our findings revealed that NaMg-GIS zeolite exhibits highly promising potential for efficient CO_2 separation, outperforming the parent Na-GIS and reference zeolites in both CO_2/CH_4 and CO_2/N_2 binary systems. Of particular importance, NaMg-GIS demonstrated an “*infinite*” selectivity for CO_2 in the CO_2/CH_4 separation at both 25 and 50°C.

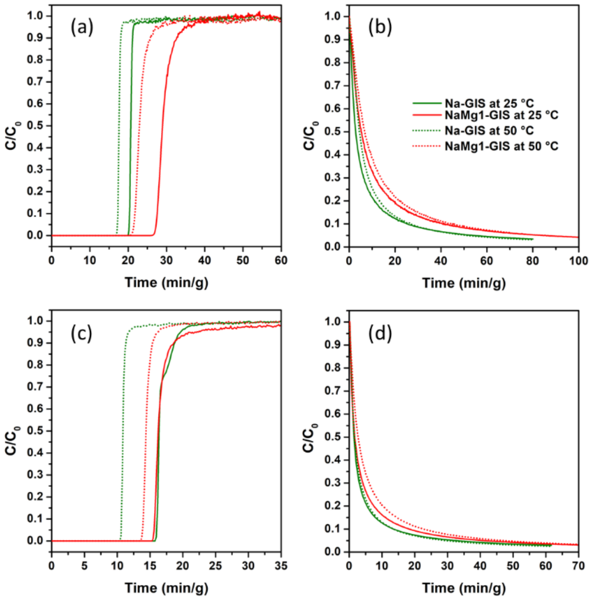


Fig. CO_2 breakthrough (a, c) and desorption curves (b, d) at 25 and 50 °C obtained from competitive dynamic adsorption experiments, $CO_2/N_2/He$, 5/25/70 (a,b) and $CO_2/CH_4/He$, 20/30/50 (c,d).

References:

1. M. Dusselier & M. E. Davis, Chemical Reviews 2018, 118 (11), 5265-5329.

Material discovery with physics and AI

Lev Sarkisov[1]

[1]The University of Manchester, UK

Email for correspondence: lev.sarkisov@manchester.ac.uk

Imagine a computer dreaming up a porous material with mathematically optimized properties for a specific application. In this presentation, I will share some ideas on how to practically realize this concept.

The exponential growth of available and hypothesized porous materials, including Metal-Organic Frameworks (MOFs), has necessitated a fundamental shift in our approach to selecting porous materials for specific applications. Computational screening methods have emerged as a necessary step to identify the most promising candidates before committing to costly experimental efforts.

Machine learning (ML) methods can significantly accelerate computational screening protocols. A typical application of ML models involves training them to predict material properties from features such as surface area or more complex characteristics, thus partially reducing the need for time-consuming molecular simulations. Essentially, the ML model facilitates the process of sifting through millions of materials to identify promising ones.

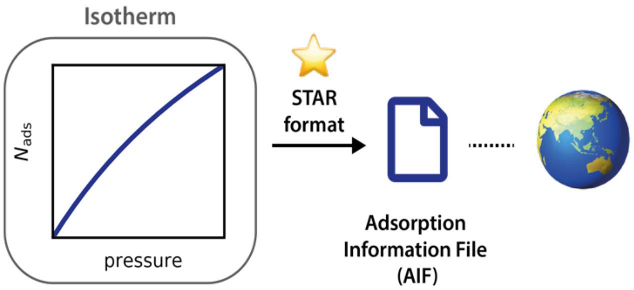
A new emerging idea is to discard direct screening approaches and instead develop methods that enable a computer to "hallucinate" new structures, guiding them towards a pre-specified objective function. This approach is not tied to any specific material database and, we speculate, could be a much more efficient way to search for materials. Implementing this idea, however, requires overcoming several challenges associated with material representation, interpretability of the model, and the physical realism of generated structures. Nonetheless, it may also create the possibility of discovering entirely new materials with unprecedented properties and novel adsorption phenomena.

Dissemination and updates to the universal standard archive file for adsorption data

Stefan Kaskel[1,4], Daniel Siderius[2], and Jack Evans[3]

[1] Dept. of Chem. & Food Chem., TU Dresden, Bergstr. 66, 01059 Dresden, Germany
[2] National Institute of Standards & Technology, 100 Bureau Dr, MS 8320, Gaithersburg 20899-8320 Maryland, USA
[3] Centre for Advanced Nanomaterials and Department of Chemistry, The University of Adelaide, Adelaide, SA 5000 Australia
[4] Fraunhofer IWS, Winterbergstr. 28, 01277 Dresden, Germany
Email for correspondence: stefan.kaskel@tu-dresden.de

Porous materials have shown remarkable effectiveness in energy and environmental applications. However, the current method of presenting adsorption isotherms through graphs and figures falls short in terms of reproducibility, reuse, and data sharing. It is crucial to promote open science in the field of porous materials for future researchers [1].



Since 2021, we have developed a novel standard adsorption information file (AIF), taking inspiration from the widely used crystallographic information file (CIF) [2]. The AIF is a versatile and easily expandable archive file format that is both human and machine-readable. We are continuously enhancing the format to meet the requirements of researchers. This initiative marks the first steps toward an open adsorption data format, simplifying the exchange of adsorption data among laboratories, journals, databases, and the scientific community. The adoption of this format is gaining momentum, driven by the support of IUPAC (https://iupac.org/project/2021-016-1-024/).

The standardized reporting of adsorption isotherms will enable the application of advanced AI methods (machine learning etc.) to develop innovative processes for separation and environmental technologies and accelerate the finding of high performance porous materials for such operations.

References:

1. Wilkinson, M. et al. The FAIR Guiding Principles for scientific data management and stewardship. Sci. Data 3 (2016) 160018.

2. Evans, J. D. et al. A Universal Standard Archive File for Adsorption Data. *Langmuir* 37 (2021) 4222-4226.

Acknowledgements:

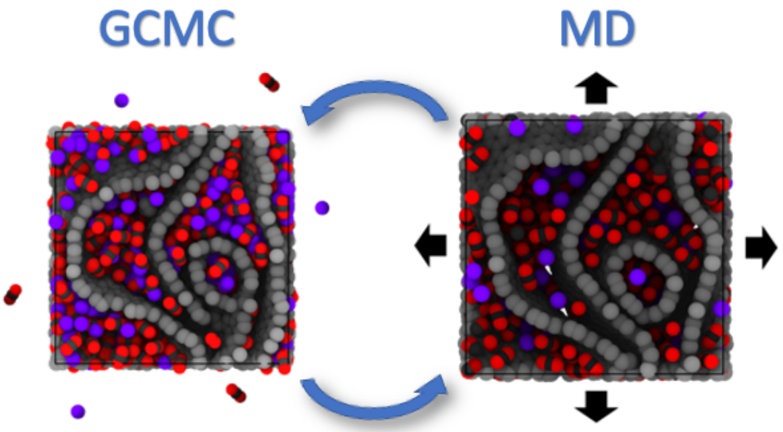
We thank IUPAC funding project 2021-016-1-024.

Applications of 3D Amorphous Carbon Molecular Models for Adsorption and Mechanical Property Predictions

Nicholas J. Corrente[a], Elizabeth L. Hinks[a], Aastha Kasera[a], Raleigh Gough[a], Peter I. Ravikovitch[b], and Alexander V. Neimark[a]

[a] Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey,
Piscataway, New Jersey 08854, United States
[b] ExxonMobil Technology and Engineering Company, Annandale, NJ, 08801, United States

We explore the capabilities of 3D molecular models of amorphous nanoporous carbons for reproducing the morphological and adsorption properties of practical activated carbons. The 3D models are generated using a reactive forcefield in molecular dynamics (MD) simulations to anneal and quench structures by mimicking the procedures used for production of practical carbons. This approach allows for the formation of corrugated and defective 3D framework built by graphene sheets. The generated structures possess tunable pore size distributions, pore volumes, and surface areas. We characterize these models by Monte Carlo (MC) simulations using standard molecular probes (CO_2, N_2, and Ar) and show that they replicate the structural properties of practical carbons. We demonstrate how the 3D models quantitatively predict adsorption of simple fluids and alkanes at experimentally relevant conditions. [1, 2] We utilize a hybrid MC/MD simulation scheme to explore how the structures deform in response to fluid adsorption. [2] The suggested method provides a thorough understanding of the effect of pore morphology and flexibility on the adsorption dynamics. This work is supported by the NSF CBET grant 1834339 and ExxonMobil.



Hybrid MC/MD simulation scheme.

References:

[1] N.J. Corrente, E.L. Hinks, A. Kasera, R. Gough, P.I. Ravikovitch, A.V. Neimark, Modeling adsorption of simple fluids and hydrocarbons on nanoporous carbons, Carbon 197 (2022) 526-533. DOI: 10.1016/j.carbon.2022.06.071

[2] F. Vallejos-Burgos, C. de Tomas, N.J. Corrente, K. Urita, S. Wang, C. Urita, I. Moriguchi, I. Suarez-Martinez, N. Marks, M. Krohn, R. Kukobat, A.V. Neimark, Y. Gogotsi, K. Kaneko, 3D Nanostructure Prediction of Porous Carbons Via Gas Adsorption, Carbon 215 (2023), 118431. DOI: 10.1016/j.carbon.2023.118431

[3] N.J. Corrente, E.L. Hinks, A. Kasera, R. Gough, P.I. Ravikovitch, A.V. Neimark, Adsorption-Induced Deformation of Nanoporous Carbons with Mixtures: A Hybrid MC/MD Approach. In preparation

Computational-aided development of MOF-based Mixed Matrix Membranes for molecular separation

Guillaume Maurin[1]

[1] Université Montpellier/CNRS

Email for correspondence: guillaume.maurin1@umontpellier.fr

Mixed matrix membranes (MMMs) incorporating MOFs into polymeric matrices show promising properties for several key gas separation processes. Understanding of the MOF/polymer interface and gas transport through the MMMs is of utmost importance. Here, we selected a series of MOFs as fillers in conjunction with both rigid and flexible polymers and we deployed our in-house computational strategy to construct MOF/Polymer atomistic models and assess their thermodynamic and dynamic adsorption properties. This computational screening revealed that the distinct characteristic of polymer backbones and MOF surfaces results in different interfacial pore structuring. We evidenced that not only size but also shape of the interfacial pore region has eminent effects on the gas transport properties of the MMMs with respect to a selected range of molecules. This conclusion is an important step toward the rational design of MMMs with the optimal interfacial pore size/shape to achieve the best performance for molecular separation. This computational strategy has been also applied recently to explore the shaping of MOFs with the selection of the appropriate polymers of crucial importance in diverse industrial applications including CO2 capture.

Molecular Simulation of Peptide Retention in Reversed-Phase Liquid Chromatography

José Paulo Mota[1]

[1] NOVA School of Science and Technology

Email for correspondence: pmota@fct.unl.pt

Reversed-phase high-performance liquid chromatography (HPLC) is a fundamental tool for the purification and analysis of peptides. Peptides are separated on a hydrophobic stationary phase and eluted with a gradient of increasing organic solvent concentration. The nonpolar stationary phases are most often spherical porous silica particles that have been surface derivatized with hydrocarbon chains 1. The conditions of reversed-phase chromatography require a nonpolar stationary phase, but this condition can be met by many different ligands. In fact, there are commercially available columns of at least C1, C2, C4, Cg, C18, phenyl, and cyano functionalities, where the carbon num- bers refer to the length of a fully saturated hydrocarbon chain. The most popular stationary phase for this purpose is an octadecyl carbon chain (C18)-bonded silica [2].

Here, we employ advanced molecular simulation techniques to explore the effect of surface density of the bonded stationary phase chains and mobile phase composition on the retention coefficients of peptides over C18-bonded silica. Chromatographic retention involves a process of solute transfer from a mobile phase into or onto a stationary phase. The association of the solute with the stationary phase can involve partitioning, adsorption, or both. In either case, transfer is characterized by an exchange of the environment at the surface of the solute molecule: solute is initially surrounded by neighboring mobile phase molecules and is finally surrounded, fully or partially, by neighboring molecules of the stationary phase. Our aim here is to consider how the standard-state chemical potentials may be predicted from the molecular structures of the peptide chain and solvents and external thermodynamic variables (silica surface derivatized with hydrocarbon chains.).

References:

1. J. G. Dorsey, K. A. Dill, Chem. Rev. 89, 331 (1989).
2. C. A. Browne, H. P. J. Bennett, S. Solomon, Anal. Biochem. 124, 201 (1982)

Structural changes in ZIFs upon gas and liquid phase adsorption

Joaquin Silvestre-Albero[1], A. Missyul,[2] A. Martín-Calvo,[3] S. Calero,[3] Judit Farrando-Perez[1]
[1] Advanced Materials Laboratory, Inorganic Chemistry Department - University Materials Institute, University of Alicante, Spain
[2]ALBA synchrotron light source, Cerdanyola del Valles, Spain
[3] Department of Physical, Chemical and Natural Systems, Universidad Pablo de Olavide, Seville, Spain

Email for correspondence: joaquin.silvestre@ua.es

Chemical contamination in water and air streams requires the design of novel adsorbents able to retain/concentrate these pollutants selectively and with a high adsorption capacity. Activated carbons, zeolites, silicas, and metal-organic frameworks are among the most frequently used adsorbents to this end. Utilizing MOFs for this purpose offers a significant advantage in terms of customization, as the pore structure and surface chemistry of these materials can be tailored to match specific applications, rendering them as highly versatile tools for adsorption processes. Among them, ZIFs, a sub-class of MOFs, are characterized by a high specific surface area, a flexible and ultra-hydrophobic pore structure and a high chemical and thermal stability [1]. These properties and the simpleness of the synthesis protocols make them ideal adsorbents for gas and liquid-phase adsorption processes. Compared to conventional adsorbents, ZIFs can suffer structural changes upon adsorption. Gate-opening, phase transition, breathing, etc., have been widely reported in the literature for ZIFs upon an external stimulus [2,3]. Despite their relevance for the adsorption performance and the selectivity of the process, structural changes in liquid-phase adsorption processes are less described. Based on these premises, the aim of this study is to identify potential structural changes in ZIFs upon liquid-phase adsorption, preferentially for aromatic contaminants, and to perform a comparative analysis with similar structural phenomena upon gas adsorption. This comparison will be achieved through the integration of adsorption studies, chemical and structural characterization techniques, modeling, as well as synchrotron-based measurements conducted prior and post-adsorption.

References:

1. R.P. Lively, M.E. Dose, J.A. Thompson, B.A. McCool, R.R. Chance, W.J. Koros, Chem. Commun., 47 (2011) 8667-8669.
2. M.E. Casco, Y.Q. Cheng, L.L. Daemen, D. Fairen-Jimenez, E.V. Ramos-Fernandez, A.J. Ramirez-Cuesta, J. Silvestre-Albero, Chem. Commun., 52 (2016) 3639.
3. J. Gandara-Loe, A. Missyul, F. Fauth, L.L. Daemen, Y.Q. Cheng, A. Ramirez-Cuesta, P.I. Ravikovitch, J. Silvestre-Albero, J. Mater. Chem. A, 7 (2019) 14552-14558.

Acknowledgements:

The authors acknowledge financial support from the MINECO (Projects PID2019-108453GB-C21 and PCI2020- 111968/ERANET-M/3D-Photocat) and European Union: Horizon Europe (project MOST-H2; Grant agreement no. 101058547).

On the characterization of nanoporous carbons with small-angle scattering

Oskar Paris[1], and Christian Prehal[2]

[1] Chair of Physics, Department Physics, Mechanics and Electrical Engineering, Montanuniversität Leoben, Franz-Josef-Strasse 19, 8700 Leoben, Austria

[2] Department of Chemistry and Physics of Materials, Paris Lodron University of Salzburg, Jakob-Haringer-Strasse 2a, 5020 Salzburg, Austria

Email for correspondence: Oskar.paris@unileoben.ac.at

Small-angle scattering of X-rays (SAXS) has long been used to characterize nanoporous materials. An advantage is that SAXS is sensitive to both, open and closed pores, and can thus deliver complementary information to gas sorption analysis (GSA). While integral parameters such as the specific pore volume or the specific surface area can readily be obtained from both methods using classical approaches, pore size distributions (PSDs) derived from the two techniques - even when comparing fully open pore systems - are usually hardly comparable on a quantitative level. Apart from the inherent difficulty of defining a "smooth" surface for, e.g., micropores with sub-nanometer pore sizes, also the shape and pore arrangement influences the results of a PSD determination. Here we show an attempt to make PSDs derived from SAXS and GSA data from a series of microporous activated carbons directly comparable [1]. To this end, a real space model of the pore structure is created from the SAXS data using the concept of Gaussian random fields. From these data, "size distributions", e.g., the distribution of normal distances from points on the surface to the opposite surface of a pore can easily be calculated. This distribution however deviates considerably from the PSD obtained from GSA data using a mixed quenched solid density functional (QSDFT) kernel due to its inherent assumption of slit like pores. A "Degree of Confinement" parameter accounting for the local pore geometry is employed to determine an alternative size distribution for purely slit like pores from the SAXS model, which shows good agreement with the corresponding GSA data. Potential applications of the approach may particularly be helpful for closed pore systems such as non-activated hard carbons.

References:

1. C. Prehal, S. Grätz, B. Krüner, M. Thommes, L. Borchert, V. Presser, O. Paris, Comparing pore structural models of nanoporous carbons obtained from small-angle scattering and gas adsorption, Carbon, 152 (2019) 416-423

Use of Ultrasonic Monitoring for In situ Diagnostics of Zeolite and MOF Crystallization

Martin Hartmann[1], Hasan Baser[2], Marcus Fischer[1], Rebecca Reber[1], and Wilhelm Schwieger[2]

[1] Institue of Chemical Reaction Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg
(FAU), Egerlandstraße 3, 91058 Erlangen, Germany
[2] Erlangen Center for Interface Research and Catalysis (ECRC), Friedrich-Alexander-Universität
Erlangen-Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany
Email for correspondence: martin.hartmann@fau.de

The investigation and understanding of the underlying mechanisms for the crystallization of molecular sieve materials such as metal-organic frameworks (MOFs) and zeolites have received increasing interest in recent years. This is mainly because improvements of the corresponding equipment were made that is essential for in situ diagnostics. In contrast to classical techniques, such as X-ray diffraction and neutron scattering, nuclear magnetic resonance or infrared and Raman spectroscopy, ultrasonic monitoring has not received proper attention [1]. Thereby, especially for zeolites, important insights have been gained with this technique already. In the present study, we report the successful use of ultrasonic device as a real-time, in-situ diagnostic tool for monitoring the crystallization progress of zeolite A from homogeneous, colloidal solutions with the composition 0.4 Na_2O : 10 SiO_2 : 1.4 Al_2O_3 : 16 $(TMA)_2O$: X H_2O (X: 650, 750, 850, 950, 1050). Kinetic information like reaction rate or reaction order of crystal growth can easily be calculated from the measured ultrasonic signal data. For the mathematical description of the crystallization curves, the experimental curves were fitted with different kinetic models. The crystallization proceeds in more than one step suggesting a change of the kinetics during the formation of the crystalline material. The evaluated reaction exponents for the different steps could only be described with Avrami-Erofeyev nucleation model. The results indicate that - depending on amount of water in synthesis mixture - first a three dimensional and then a one dimensional crystal growth takes place.

The understanding of metal organic framework syntheses is still a challenging task in the field of porous materials. Proposed models for the MOF formation mechanisms includes the formation of pre-nucleation building units (PNBU), which are “the minimum assembly of atoms, ions or molecules which, by condensation of the group with others (identical or different) give rise to the final solid” [2]. The nature of these PNBUs is widely discussed, but detailed insights are still rare. In this study, ZIF-8 with varying particle size and morphology is synthesized from zinc nitrate hexahydrate, 2-methylimidazole and CTAB in different solvents. In our study, we found that the ultrasonic attenuation already increases rapidly within the first minute of the ZIF-8 syntheses. Depending on the molar ratio of linker to metal, not only the final particle size, but also the course of the ultrasonic signal changes. After stopping the syntheses at different times of during the attenuation increase, it can be seen that in the synthesis with higher linker excess a second phase, namely ZIF-L is formed in the first three minutes, while in the synthesis with an antilogarithmic course of attenuation $HMIM/Zn^{2+} = 60$ only reflexes of ZIF-8 and the linker are visible.

References:

1. M. Ermer, R. Reber, H. Baser, M. Fischer, W. Schwieger, M. Hartmann, Perspective on the Use of Ultrasonic Monitoring for In Situ Diagnostics of Zeolite and MOF Crystallization, Cystal Growth & Design 23 (2023) 3795-3807 (2023)
2. H. Embrechts, M. Kriesten, M. Ermer, W. Peukert, M. Hartmann, M. Distaso, Role of Prenucleation Building Units in Determining Metal-Organic Framework MIL-53(Al) Morphology, Crystal Growth & Design, 20 (2020) 2631–3649.

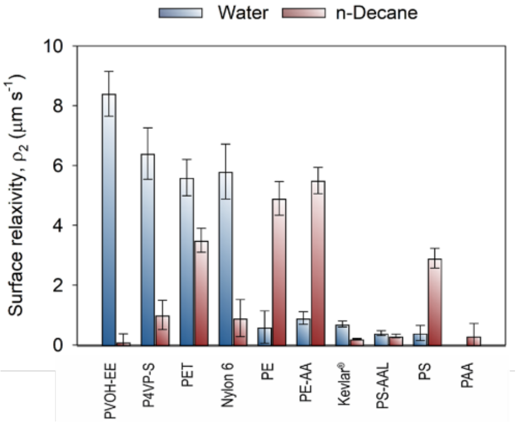
Correlations of NMR Relaxometry Data and Polymer Surface Chemistry

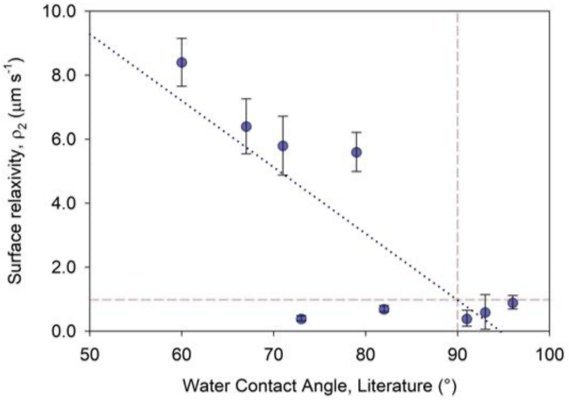
Murilo T. Suekuni[1] and Alan M. Allgeier[1]

[1] Dept. of Chem. & Petrol. Eng., University of Kansas, Lawrence, KS 66045 USA
Email for correspondence: alan.allgeier@ku.edu

Nuclear magnetic resonance (NMR) relaxometry enables facile characterization of a variety of porous materials filled with liquids and gases. This study identifies quantitative correlations between surface chemistry and NMR relaxation rates for a series of polymeric particle dispersions, serving as well controlled examples of surface fluid interactions [1].

In NMR relaxometry, the measurement of the rate at which certain nuclei, e.g., ^{1}H, re-equilibrate with an externally applied magnetic field upon radio-frequency excitation provides insight about pore size and pore surface chemistry. A solid-fluid affinity parameter (surface relaxivity, ρ_2), linearly regressed from transverse relaxation data, reflects the constrained motion of adsorbate molecules interacting with surfaces. Despite the increasing interest by the characterization community, the role of surface chemistry upon the characterization of wetted surface area and pore volume distribution using solvent relaxometry remains underexplored. D'Agostino et al. have correlated adsorption strength [2] and Schlumberger et al. have correlated water intrusion [3] to relaxation data for silica surfaces. The present study explores wide-ranging polymer particle surface chemistry from hydrophobic polyethylene to hydrophilic polyacrylic acid suspended in water and decane. The observed trends showed a positive relation between heteroatom (oxygen, nitrogen) content and interactions with water, with an opposite behavior for n-decane. This work supports the development of a transverse surface relaxivity database, with values ranging from 0.1 to 8.4 µm s^{-1} and notable correlations to water contact angles. Ongoing investigation indicates that relaxometry has promising applications in various fields, including heterogeneous catalysis, petroleum reservoir exploration, and drug delivery mechanisms.





References:

1. M.T. Suekuni, A.M. Allgeier. Correlating Surface Chemistry to Surface Relaxivity via TD-NMR Studies of Polymer Particle Suspensions. JACS Au. 3 (2023) 2826-34.
2. C. D'Agostino et al. Interpretation of NMR Relaxation as a Tool for Characterising the Adsorption Strength of Liquids inside Porous Materials. Chemistry - A European Journal, 20 (2014) 13009–13015.
3. C. Schlumberger, M. Thommes and coworkers. Characterization of functionalized chromatographic silica materials: Coupling water adsorption and intrusion with NMR-relaxometry . ChemRxiv. Cambridge: Cambridge Open Engage; 2023. https://10.26434/chemrxiv-2023-jmjs8-v3

Advanced Textural and Surface Chemistry Characterization by Combining Adsorption and Liquid Intrusion with NMR Relaxometry

Carola Schlumberger[1]; Carlos Cuadrado Collados[1]; Jakob Söllner[1]; Lukas Sandner[1]; Jincheng Xu[1]; Matthias Thommes[1]

[1] Institute of Separation Science and Technology, Friedrich-Alexander-University Erlangen-Nuremberg

Emails for correspondence: matthias.thommes@fau.de, jincheng.xu@fau.de, carola.schlumberger@fau.de, jakob.soellner@fau.de, carlos.cuadrado@fau.de, lukas.sandner@fau.de

During the last decades, major progress has been made concerning the synthesis of nanoporous materials allowing for the custom design of nanoporous materials for targeted applications in various areas such as chromatography or catalysis. Enhancing the efficiency of these processes requires the tuning of the selectivity of the porous material to certain compounds of interest. Textural properties, such as the specific surface area and pore (entrance) size may affect the process efficiency. Within this context, we have recently shown that NMR relaxometry can be developed into a methodology for surface area assessment of nanoporous materials immersed in a liquid phase. We also demonstrated that NMR relaxometry shows potential to be developed as novel methodology for fast determination of pore entrance sizes. In this sense, the choice of probe molecules with varying kinetic diameters enables one to get information about the pore entrance size due to their different accessibility to the pore system 1.

In addition to textural properties, the surface chemistry plays an important role since it can enhance the affinity and selectivity of certain compounds. The design of these processes therefore requires the detailed investigation of the relation between structural properties, surface chemistry and the resulting process performance. Hence, reliable surface chemistry characterization of porous materials is crucial.

In this context, the quantification of the surface chemistry inside of pores is very challenging and usually requires a combination of different experimental tools. Within this context, we demonstrate that NMR relaxometry can be a valuable complementary tool for the fast characterization of the surface chemistry of nanoporous materials. The ratio of the spin-lattice to spin-spin relaxation time (T_1/T_2) has been suggested for surface chemistry and wettability characterization in the past. However, the relaxation time ratio of a certain sample may be affected by the surface chemistry as well as textural properties such as the surface area and pore size. Hence, quantification and comparison of the surface chemistry of different nanoporous materials is challenging. To address this limitation, this study suggests a novel methodology for surface chemistry and wettability quantification based on the ratio of the spin-spin to spin-lattice surface relaxivity, which can be related to the spin-lattice to spin-spin relaxation time ratio of the adsorbed liquid film on the pore surface ($T_{1,ads.film}/T_{2,ads.film-ratio}$). This novel approach allows for the determination of a characteristic value, which is solely affected by the surface chemistry. This is demonstrated using mesoporous stationary phase materials functionalized with different hydrophilic and hydrophobic surface functional groups. The study shows, for the first time, the correlation between the $T_{1,ads.film}/\ T_{2,ads.film-ratio}$ of water and the contact angle of the adsorbed water film determined with water vapor adsorption and water intrusion.

References:

1. C. Schlumberger, L. Sandner, A. Michalowski, M. Thommes. Reliable Surface Area Assessment of Wet and Dry Nonporous and Nanoporous Particles: Nuclear Magnetic Resonance Relaxometry and Gas Physisorption. Langmuir 2023, 39 (13), 4611–4621.

Brain Tissue Modeled as a Porous Medium with parameters derived from Micro-Iontophoresis Experiments

Charles Nicholson[1]

[1]Dept. Neuroscience and Physiology, New York University School of Medicine, 435 E 30th St., New York, NY 10016, USA
Email for correspondence: charles.nicholson@nyu.edu

The cellular structures of the brain are separated by a narrow fluid-filled extracellular (interstitial) space giving brain tissue properties of a porous medium. The porosity and tortuosity can be measured by releasing tetramethylammonium cations from a micropipette and measuring the time-dependent concentration about 100 µm away using an ion-selective microelectrode (ISM), as shown in Fig. 1 [1].

Fitting the results of experiments to an appropriate solution to the diffusion equation [1, 2] revealed that that the typical **porosity is $\phi \sim$ 0.2** and the **tortuosity is $\tau \sim$ 1.6**, where tortuosity = $(D/D^*)^{0.5}$, D is free diffusivity and D^* is effective diffusivity. These results were modeled by regarding the brain as an ensemble of cubic cells of side $2a$ with cubic voids (expansions of interstitial space) of side b at each corner. Cells were separated by sheets of interstitial space of width $2w$ and the packed cells formed composite voids of width $2b$, as shown in Fig. 2.

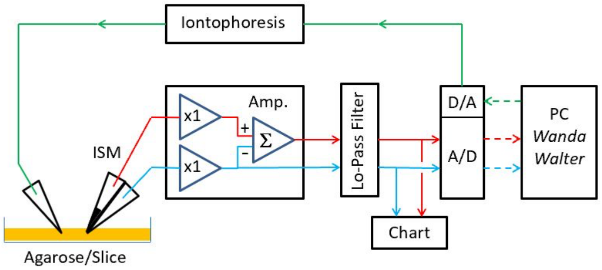


Fig.1. Experimental setup. Diffusion measurements made in agarose (D) or brain slice (D^*). Analysis with custom MATLAB software (Wanda and Walter) [1].

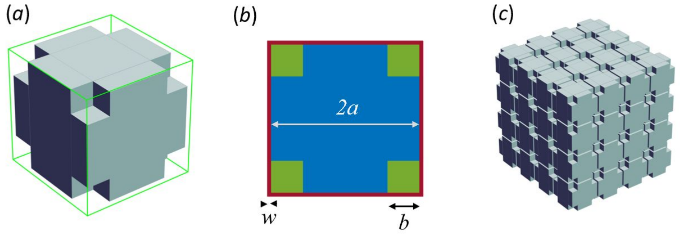


Fig. 2. Model of brain tissue. (*a*) unit cell with cubic corner voids. (*b*) top view of cell (*c*) ensemble of cells spaced $2w$ apart. In practice, 32^3 or 64^3 cells used for Monte Carlo simulations

Monte Carlo simulations took place in this ensemble using the MCell program [3]. It was found that, to obtain the experimental ϕ and τ, the required geometry was **a = 0.742 µm, b = 0.379 µm and w = 20** nm [4]. The presence of voids was essential to obtain the measured tortuosity and this feature was consistent with freeze-fixed electron microscopy and super resolution optical imaging [4].

References:

1. J. Odackal, R. Colbourn, N. J. Odackal, L. Tao, C. Nicholson, and S. Hrabetova. Real-time iontophoresis with tetramethylammonium to quantify volume fraction and tortuosity of brain extracellular space, *JoVE*: e55755 (2017).
2. E. Syková, and C. Nicholson. Diffusion in brain extracellular space, *Physiological Reviews*, 88 (2008) 1277-1340.
3. J.R. Stiles, and T.M. Bartol. 2001. Monte Carlo methods for simulating realistic synaptic microphysiology using MCell. in E. De Schutter, Editor, Computational Neuroscience: Realistic Modeling for Experimentalists, CRC Press: London; 2001, p 87 - 127.
4. C. Nicholson, Sheet and void porous media models for brain interstitial space, *Journal Royal Society Interface*, 20 (2023): 20230223.

3-D Density Functional Reory to Describe Adsorption of Pure Substances and Their Mixtures on Crystalline and Amorphous Adsorbents

Frederico Wanderley Tavares[1]

[1]Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

Email for correspondence: tavares@eq.ufrj.br

The 1-D, 2-D, and 3-D classical Density Functional Theory (cDFT) consistent with the PC-SAFT equation of state are used to investigate the adsorption isotherms and local densities of pure hydrocarbons, H2, and CO2 and their mixtures in crystalline-structure materials (like MOF-5) and amorphous materials (like nanoporous carbons). The cDFT calculations reveal that the adsorption process is influenced by the fluid-fluid spatial correlations between the fluid molecules and the external potential produced by the solid structure. These findings are supported by a comparison with experimental data and Grand Canonical Monte Carlo (GCMC) simulations of the adsorbed amount and density profiles of the adsorbed fluid inside the solid. One important parameter related to the accuracy involved in the DFT calculations is choosing the appropriate grid size. We proposed a priori grid size that is crucial in 3-D-DFT calculations. We also explore the impact of the non-crystalline structure of amorphous carbon nanopores on fluid structure and adsorption isotherms, as well as fluid-fluid and fluid-solid interactions. We offer insights for selecting computational methods in the fluid-structure analysis of nanoporous materials, guiding future research and optimization in advanced material development for diverse applications.

References:

1) Lucas J. dos Santos, Vítor M. Sermoud, Amaro G. Barreto Jr., Frederico W. Tavares, "Adsorption-Induced Deformation of Nanoporous Carbons: Insight from Classical Density Functional Theory Based on the PC-SAFT Equation of State," Fluid Phase Equilibria, 574, 113882 (2023).
DOI: 10.1016/j.fluid.2023.113882

2) Elvis Soares, Amaro G. Barreto Jr., Frederico W. Tavares, "Classical Density Functional Theory Reveals Structural Information of H2 and CH4 Fluids Adsorption in MOF-5", Fluid Phase Equilibria, 574, 113887 (2023).
DOI: 10.1016/j.fluid.2023. 113887

3) Lucas J. dos Santos, Elvis Soares, Amaro G. Barreto Jr., Frederico W. Tavares, "Comparison of 3D-cDFT and GCMC Simulations for Fluid-Structure Analysis in Amorphous Carbon Nanoporous Materials", Adsorption, (2024). Submitted.

A non-local Density Functional Theory for water adsorbed in nanoporous materials.

Antoine Barthes[1], David Grégoire[1] and Christelle Miqueu[1]

[1] Université de Pau et des pays de l'Adour, CNRS, LFCR (UMR 5150), Mechanics and Physis in Porous Media group, 1 allée du parc Montaury, Anglet, France

Email for correspondence: christelle.miqueu@univ-pau.fr

Water confined in nanoporous materials has focused many attentions due to its vast number of technical applications and scientific fields such as geosciences, biology, catalysts, gas separation, *etc* [1,2 Indeed, confinement of water in nanopores affects its thermodynamic properties such as its density, its freezing temperature, the crystal structure, *etc*. For some years now, porosimeter manufacturers have been integrating the ability to perform high-precision measurements of adsorption of vapors at low pressure, including water. In parallel, thermoporosimetry appears to be a good alternative - or at least a good complementary technique - to gas porosimetry and mercury intrusion, especially for the investigation of the samples that can be destroyed in drying process [3]. The common features between water vapor sorption analysis and thermoporosimetry is that a reliable model of water adsorption inside nanopores is necessary to interpret the experimental data and try to obtain structural information of the porous materials from these measurements. In this work, we present a new NLDFT framework for confined water based on the general formulation of Wertheim's thermodynamic perturbation theory [4] and the statistical associating fluid theory [4]. The resulting model can be employed to determine the microscopic structure of inhomogeneous water in pores of arbitrary 3D geometry. It is first used to compute the density distribution, adsorbed amount, hydrogen bonding, pore pressure, adsorption-desorption behavior at pore scale. Then, the information is upscaled to compute water adsorption isotherms in microporous adsorbents and compare them with experimental data.

References:

1. Zangi, R., Water confined to a slab geometry: a review of recent computer simulation studies, Journal of Physics: Condensed Matter, 16(45) (2004) S5371–S5388.
2. Giovambattista, N.; Rossky, P. J.; Debenedetti, P. G., Computational Studies of Pressure, Temperature, and Surface Effects on the Structure and Thermodynamics of Confined Water, Annual Review of Physical Chemistry. Annual Reviews, 63(1) (2012) 179–200.
3. Majda, D.; Zimowska, M.; Tarach, K.; Góra-Marek, K.; Napruszewska, B. D.; Michalik-Zym, A., Water thermoporosimetry as a tool of characterization of the textural parameters of mesoporous materials: Refinement of the methodology, Journal of Thermal Analysis and Calorimetry, 127 (2017) 207-220.
4. M. S. Wertheim, Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations, J. Stat. Phys., 35 (1984) 35–37.
5. G. Jackson; W. G. Chapman; K. E. Gubbins, Phase equilibria of associating fluids spherical molecules with multiple bonding sites, Mol. Phys., 65 (1988) 1–31.

Acknowledgements:

E2S UPPA hub Newpores supported ANR (ANR-16- IDEX-0002) are acknowledged for the funding of this project and A. Barthes PhD grant.

Coupling between poroelasticity and the density functional theory for the estimation of adsorption-induced swelling in nanoporous materials

Youssef Khaldouni[1], Laurent Perrier[1], Thomas Bernet[2], Christelle Miqueu[1] and David Grégoire[1]

[1] Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France [2]
Department of Chemical Engineering, Imperial College London, UK
Email for correspondence: david.gregoire@univ-pau.fr

Natural and synthesised porous media are generally composed of a double porosity: a microporosity where the fluid is trapped as an adsorbed phase and a meso- or a macroporosity required to ensure the transport of fluids to and from the smaller pores. In nanometer-scale pores, the molecules of fluid are confined. This effect induces that fluid-fluid and fluid-solid interactions sum at the pore scale and have significant consequences at the macroscale, such as instantaneous deformation, which are not predicted by classical poromechanics. If adsorption in nanopores induces instantaneous deformation at a higher scale, the matrix swelling may close the transport porosity, reducing the global permeability of the porous system.

This contribution aims at modelling the linear poroelastic behavior of isotropic porous media saturated with an adsorbable fluid. A poromechanical model is coupled with the molecular density functional theory (DFT) and experimental comparisons are performed in term of excess adsorption isotherms and induced strain in an activated carbon saturated with methane and carbon dioxide.

First, a version of non-local DFT [1] coupled with SAFT-VR-Mie state equation is used for the estimation of the adsorption of methane (CH4) and carbon dioxide (CO2) on an activated carbon. For this purpose, the material is firstly characterized by argon porosimetry at 87K to determine its pore size distribution (PSD).
Thereafter, the adsorbed quantities at the pore scale are estimated for CH4 and CO2 respectively at 303K and 318K. The upscaling is performed through the PSD, so the adsorption isotherms are obtained and compared to experimental measurements [3].

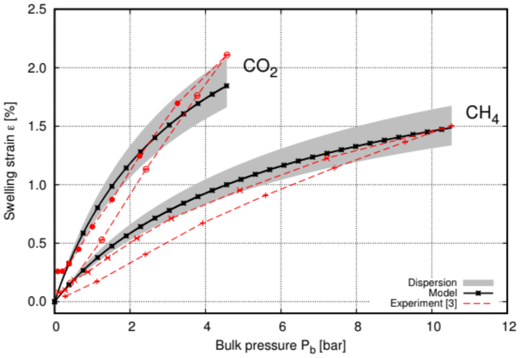


Figure 1. Comparison between swelling strain experimentally measured and estimated by the model for CH_4 and CO_2 adsorption on an active carbon.

Then, the classical poroelasticity theory is extended to consider the fluid confinement effects [2] at the nanoscale based on the DFT-SAFT estimation of the global adsorption isotherm. The estimated deformationis in good agreement with experimental measurements [3] without any fitting parameter (see Figure 1).

References:

1. Bernet, T., Müller, E.A. and Jackson, G. (2020). J. Chem. Phys. 152 (22), 224701.
2. Perrier, L., Pijaudier-Cabot, G. and Grégoire, D. (2018). Int. J. Solids Struct. 146, 192-202.
3. Perrier, L., Plantier, F. and Grégoire, D. (2017). Rev Sci Instrum 88 (3), 035104.

Acknowledgements:

This work is partially financed by the Institut Carnot ISIFOR and the Investissement d'Avenir French programme
(ANR-16-IDEX-0002) under the framework of the E2S UPPA hub Newpores

Framework-dependent kinetics of adsorption-induced structural transition in flexible metal-organic frameworks

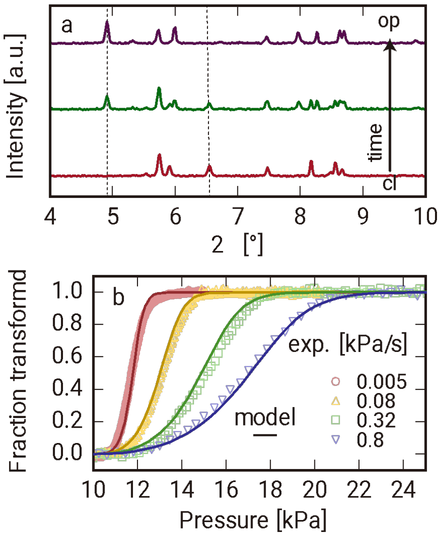
Shotaro Hiraide,[1] Yuta Sakanaka,[1] Iori Sgawara,[1] Hajime Uematsu,[1] Shogo Kawaguchi,[2] Minoru T. Miyahara[1] and Satoshi Watanabe[1]

[1] Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan
[2] Japan Synchrotron Radiation Research Institute, SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan
Email for correspondence: hiraide@cheme.kyoto-u.ac.jp

Flexible metal–organic frameworks (MOFs) exhibit a guest-induced structural transition upon gas adsorption, called "gate opening" or "breathing," and are expected to be applied to gas separation processes due to their high selectivity and stepwise change in the amount adsorbed. [1] While the mechanism of the adsorption-induced structural transition has been explained by thermodynamics, [2] the kinetic nature of the structural transition has not been fully investigated. In this study, we aimed to elucidate the dynamics of the structural transition on ELM-11 ($[Cu(BF_4)_2(4,4'\text{-bipyridine})_2]_n$) induced by CO_2 adsorption using time-resolved in situ X-ray powder diffraction (TRXRD) measurements.

The TRXRD patterns of ELM-11 during CO_2 gate opening were continuously obtained with 0.5 s exposure for each data at SPring-8, Japan. During the measurements, the CO_2 pressure was increased with constant pressurization rates at 0.005, 0.08, 0.32, and 0.8 kPa/s, and the temperature was controlled at 223, 248, and 273 K.

Fig. 1a shows the TRXRD patterns at 248 K and 0.80 kPa/s. All of the patterns have peaks belonging to the closed state (cl) and/or peaks belonging to the open state (op), which indicates the absence of an intermediate phase. Thus, the fraction transformed α was determined from the intensity ratio of op to cl (Fig. 1b). A detailed analysis of the measured data revealed that the transition rate could be expressed as the difference between the gas pressure and the gate-opening pressure ($P - P_g$) multiplied by the autocatalytic reaction model ($(k_1\alpha + k_2)(1 - \alpha)$), which is in good agreement with the experimental results. (solid lines in Fig. 1b). The autocatalytic reaction model of ELM-11 was found to reflect the existence of two pathways for CO_2 penetration in the framework. Moreover, the same analysis was conducted for CO_2 breathing in MIL-53(Al) ($[Al(OH)(1,4\text{-benzendicarboxylate})]_n$) and CO_2 gate opening in CuFB ($[Cu(\text{fumarate})(\text{trans-bis(4-pyridyl)ethylene})_{0.5}]_n$), revealing that their structural transition rates are modeled by first-order model and zero-order model. This result confirmed that the adsorption kinetics of flexible MOFs is highly dependent on their framework structure. [3]



References:

1. S. Hiraide et al., Nat. Commun. **11,** 3867 (2020).
2. F. X. Coudert et al., J. Am. Chem. Soc. **130,** 14294 (2008).
3. Y. Sakanaka et al., Nat. Commun. **14,** 6862 (2023).

Impact of a kerogen network on the behavior of confined hydrocarbon liquids

Dmitry N. Lapshin[1], Bennett D. Marshall[2], Peter I. Ravikovitch[2], Erich A. Muller[1,*]

[1] Department of Chemical Engineering, Imperial College London, United Kingdom
[2] ExxonMobil Research and Engineering Company, Annandale, New Jersey, United States
Email for correspondence: e.muller@imperial.ac.uk

Kerogen is an intrinsically complex, heterogeneous, and disordered material [1]. Depending on its geological origin and maturity, the chemical composition of kerogen may vary significantly along with its structural properties, such as the cross-link density of the network and its intrinsic porosity [2]. Furthermore, upon hydrocarbon migration in shales, extraction, and adsorption, the cross-linked networks dynamically change, making the experimental and modelling of this porous media very challenging.

This work presents recent advances in utilizing molecular dynamics simulations to explore the adsorption and transport of high-pressure liquid hydrocarbons such as toluene, cyclohexane, and n-decane and their impact on the dynamic behavior of a kerogen nanostructure. Kerogen structures are developed following a mimetic algorithm using chemically-accurate coarse-grained models. We postulate that kerogen structures can be assembled as a combination of aliphatic and aromatic molecular building blocks such as n-dodecane, triphenylene, benzopyrene, perylene, and coronene [3]. Combining these molecules and adopting the SAFT force field [4] for their coarse-grained models, we generate fully cross-linked structures representative of four types of kerogens of different maturity, including 1A, 2B, and 2D. The models are validated against available experimental data and in-silico data [3]. The developed CG models offer a unique platform for studying thermodynamic and transport properties of hydrocarbon fluids.

This work presents recent advances in utilizing molecular dynamics simulations to explore the adsorption and transport of high-pressure liquid hydrocarbons such as toluene, cyclohexane, and n-decane and their impact on the dynamic behavior of a kerogen nanostructure. Kerogen structures are developed following a mimetic algorithm using chemically-accurate coarse-grained models. We postulate that kerogen structures can be assembled as a combination of aliphatic and aromatic molecular building blocks such as n-dodecane, triphenylene, benzopyrene, perylene, and coronene [3]. Combining these molecules and adopting the SAFT force field [4] for their coarse-grained models, we generate fully cross-linked structures representative of four types of kerogens of different maturity, including 1A, 2B, and 2D. The models are validated against available experimental data and in-silico data [3]. The developed CG models offer a unique platform for studying thermodynamic and transport properties of hydrocarbon fluids.

References:

1. E. Rezlerová, S. K. Jain, M. Lísal, Adsorption, Diffusion, and Transport of C1 to C3 Alkanes and Carbon Dioxide in Dual-Porosity Kerogens: Insights from Molecular Simulations, *Energy Fuels*, **37**, 492-508, 2023.
2. D. Ertas, S. R. Kelemen, T. C. Halsey, Petroleum Expulsion Part 1. Theory of Kerogen Swelling in Multicomponent Solvents, *Energy & Fuels*, **20**, 295-300, 2006.
3. P. Ungerer, J. Collell, M. Yiannourakou, Molecular Modeling of the Volumetric and Thermodynamic Properties of Kerogen: Influence of Organic Type and Maturity, *Energy Fuels,* **29**(1), 91-105, 2015.
4. E. A. Müller and G. Jackson, Force-Field Parameters from the SAFT-γ Equation of State for Use in Coarse-Grained Molecular Simulations, *Annu. Rev. Chem. Biomolec. Eng.*, **5**, 405-427, 2014.

CPM9 | REPORT OF ABSTRACTS

WEDNESDAY, MAY 22, 2024

Structure characterization-mediated designing of novel carbon-based nanostructured materials

Katsumi Kaneko[1]

[1]Research Initiative for Supra-Materials, Shinshu University, Nagano, Japan
Email for correspondence: kkaneko@shinshu-u.ac.jp

Carbon has outstanding physical properties such as high electrical conductivity and excellent mechanical strength and chemically and physically robustness. The nanostructured carbon such as nanoporous carbons, single wall carbon nanotube (SWCNT) and graphenes have promising potentials for giving solutions to the global warming issue. This presentation introduces the importance of structural characterization in the following four key topics.

The supercapacitors using ionic liquid (IL)s can realize very high energy density. The structure of ionic liquid, EMI-TFSI, in 0.7 nm pores of carbide-derived carbon was studied with HRMC simulation-aided X-ray scattering. We evidenced the partial breaking of Coulombic law for the assembly structure of IL ions[1].

The ambient pressure storage of high density methane in nanoporous carbons enables to develop convenient methane cartridges irrespective of the severe difficulty[2]. We coated nanoporous carbon with graphenes which have a thermally switchable valve function. The nanographene valves open at 473 K and close at ambient temperature[3]. The stored methane of large amount can be stably stored for two weeks at least.

The mechanical energy storage using multi-wall carbon nanotube was reported by Baughman et al[4]. However, their stored energy is not necessarily remarkable. We prepared the SWCNT ropes which have the gravimetric energy density (GED) of up to 2.1 MJ kg^{-1} exceeding by over four orders of magnitude that of mechanical steel springs and by a factor of 3 that of advanced LIBs in addition to the low temperature stability[5].

Ultrafast-permeable graphene-wrapped crystal membranes which give an excellent separation ability, as evidenced by marked upward-deviation from the upper bound of Robeson plot for H_2/CH_4. The graphene-wrapped zeolites[6] have the subnanoscale channels of < 0.4 nm in width between graphene and their crystal faces, which induce a high selectivity.

References:

1). R. Futamura, T. Iiyama, Y. Takasaki, Y. Gogotsi, M. J. Biggs, M. Salanne, J. Ségalini, P. Simon, K.Kaneko, (2017) *Nature Mater*. 16, 1163-1273.

2). K. Kaneko and F. Rodriguez-Reinoso Eds. (2019) *Nanoporous Materials for Gas Storage*, Chaps. 2 and 3, Springer,

3). S. Wang、F. Vallejos-Burgos, A. Furuse, J. P. Marco-Lozar, M. Nagae, H. Tanaka, H. Kanoh, J. Silvestre-Albero, T. Hayashi, K. Kaneko. *Nature Energy*, In revision

4). M. Zhang, W.Cai, Z. Wang, S. Fang, R. Zhang, H. Lu, A. E. Aliev, A. A. Zakhidov, C. Huynh, E. Gao, J. Oh, J. H. Moon, J. W. Park, S. J. Kim, R. H. Baughman, (2023) *Nature Energy*, 8, 203-213.

5). S. Utsumi, S. Kumar, S. Takahashi, R. Shimodomae, T. Yamura, R. Okuda, R. Kobayashi, O.Takahashi, S. Miyazono. P. Ahuja, A. Furuse, D. Tomanek, K. Kaneko, *Nature Nanotech*. In second revision.

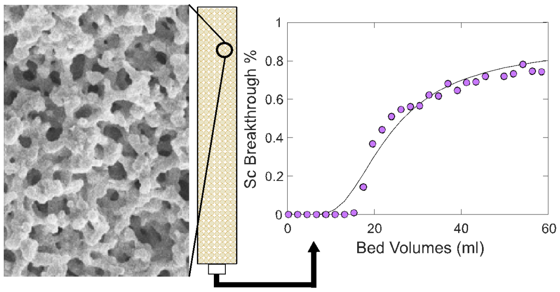
6). R. Kukobat, M. Sakai, H. Tanaka, F. Vallejos- Burgos, C. Lastoskie, M. Matsukata, Y. Sasaki, K. Yoshida, T. Hayashi, K. Kaneko, (2022) *Sci. Adv.* 8, eabl3521 (1-11).

Designing Macroporous-Mesoporous Adsorbents for Sustainability

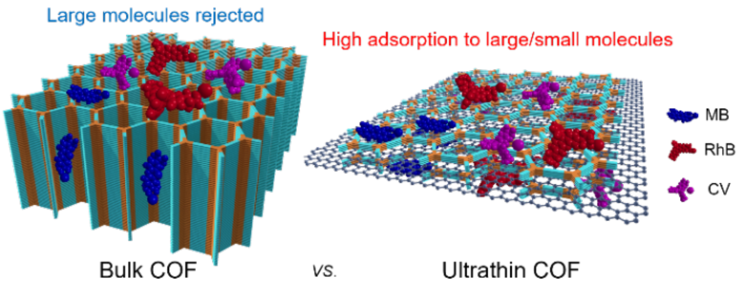
Freddy Kleitz[1], Aaron Brewer[1], Changxia Li[1], Patrick Guggenberger[1] and Justyna Florek[1]

[1]Department of Functional Materials and Catalysis, Faculty of Chemistry, University of Vienna,
Währinger Strasse 42, 1090, Vienna, Austria
Email for correspondence: freddy.kleitz@univie.ac.at

Nanoporous materials offer significant advantages for application as selective sorbents, catalysts or nanocarriers for biomedical technologies, owing to their high specific surface area and well-calibrated pores large enough to perform reactions or processes involving adsorption and diffusion of bulky species. Here, we discuss synthesis concepts for the design of functional nanoporous materials containing both mesopores and macropores, that could offer interesting prospects for separation technologies. Emphasis is placed on hierarchically-porous monolith and powder sorbents for critical materials recovery and pollutant removal.



Monolithic macroporous-mesoporous silica generally exhibits high surface area for adsorption, and silica monoliths display exceptional adaptability, due to the range of options for functionalization and excellent tunability in terms of pore size, pore volume, and framework structure. Furthermore, hierarchically-porous monoliths have superior mass transport properties compared to traditional particulate adsorbents.[1] This attribute permits large volumes of feedstock to be rapidly processed through the sorbent, greatly elevating the potential scalability of the system, circumventing issues such as pressure buildup and column clogging. Recently, we described a way to use designed (powdered) hierarchically porous monoliths in practical, scalable metal extraction systems. We apply the sorbents in continuous flow columns for Scandium extraction at conditions realistic for industrial use (Fig 1).[2]



Covalent organic frameworks (COFs) are also of great potential as adsorbents owing to their tailorable functionalities, low density, and high porosity. However, their intrinsically stacked 2D structure limits the full use of their surface for sorption, especially the internal pores. The construction of ultrathin COFs could increase the exposure of active sites to the targeted molecules in a pollutant environment. We show that an ultrathin COF can be prepared with uniform thickness of ca. 2 nm employing graphene as the surface template [3]. The resulting hybrid aerogel with ultralow density (7.1 mg cm^{-3}) has the ability to remove organic dyes of different sizes with high efficiency (Fig. 2). The 3D macroporous structure and well-exposed adsorption sites permit rapid diffusion and efficient adsorption of organic pollutants, greatly contributing to an enhanced uptake capacity.

References:

1. A. Brewer, J. Florek, F. Kleitz, A Perspective on Developing Solid-Phase Extraction Technologies for Industrial-Scale Critical Materials Recovery, Green Chem. 24 (2022) 2752-2765.
2. A. Brewer, C. Reicher, O. Manatschal, H. Bai, K. Nakanishi,,F. Kleitz, Powdered Hierarchically Porous Silica Monoliths for the Selective Extraction of Scandium, ACS Sustainable Chem. & Eng. 11 (2023) 15432-15439.
3. C. Li, P. Guggenberger, S. W. Han, W. L. Ding, F. Kleitz, Ultrathin Covalent Organic Framework Anchored on Graphene for Enhanced Organic Pollutant Removal, Angew. Chem. Int. Ed. 61 (2022), e202206564.

Acknowledgements:

The authors thank the funding support of the FWF and the University of Vienna, Austria.

Tuneable mesoporous silica materials for gas storage applications via nanoconfined clathrate formation

Pegie Cool[1]

[1]Laboratory of Adsorption and Catalysis, Department of Chemistry, University of Antwerp,
Universiteitsplein 1, B-2610 Wilrijk, Belgium

Email for correspondence: pegie.cool@uantwerpen.be

The safe storage and utilisation of gases, such as hydrogen, is an ongoing research area and has the potential to promote hydrogen as a major substitute for carbon-based fuels. Clathrates (gas hydrates) are water-based crystal structures (ice-like) able to trap hydrogen or methane molecules in the cages formed by the scaffold arrangements. As only water is required for the construction of the cages, the clathrates have been identified as a potential solution for safe gas storage. However, as the pure gas clathrate still requires harsh synthesis conditions, we propose an approach which exploits the extraordinary change of the water properties when confined in a nano-space. Specifically, it will be shown that a hydrophobic mesoporous silica can act as the nano-confinement for the ice-like hydrate. The research presented focuses on the possible surface chemistry effect of mesoporous silicas, as well as the pore network influencing the clathrate formation, showcasing applications of CH_4 and H_2 gas storage.

For example, a hydrophobized SBA-15 is demonstrated to promote methane hydrate formation [1]. In comparison to as-synthesized SBA-15, hydrophobization by C_8-grafting accelerates the kinetics of methane storage in and delivery from the hydrate. X-ray diffraction demonstrates formation of Structure I hydrate on SBA-15 C8. At 7.0 MPa and 248 K, the water-to-hydrate conversion on hydrophobized SBA-15 C8 reaches 96% as compared to only 71% on a pristine SBA-15 sample with comparable pore size, pore volume and surface area. Fast loading and unloading of methane on the modified silica was achieved in 19 subsequent cycles without losses in kinetics.

A Mesoporous Cellular Foam (MCF) grafted with a THF like functional group was tested for H_2 hydrate formation at 7 MPa, 262-268 K under 100% pore volume saturation of 5.56 mol% THF solution [2]. The materials exhibit rapid hydrate formation, and the THF-like functionalized MCF material showed an excellent promoting effect on H_2 storage compared to non-functionalized material MCF despite having a pore-volume ≈ 16% and 24% lower than MCF, respectively.

References:

1. E.J. Beckwée, M. Houlleberghs, R-G Ciocarlan, C. V. Chandran, S. Radhakrishnan, L. Hanssens, P. Cool, J. Martens, E. Breynaert, G.V. Baron, J.F.M. Denayer, Structure I methane hydrate confined in C_8-grafted SBA-15: a highly efficient storage system enabling ultrafast methane loading and unloading, Applied Energy 353 (2024) 122120.
2. N. B. Kummamuru, G. Watson, R.-G. Ciocarlan, S.W. Verbruggen, P. Cool, P. Van Der Voort, P. Perreault, Accelerated methane storage in clathrate hydrates using mesoporous (organo) silica materials, Fuel 354, (2023) 129403.

Acknowledgements:

P. Cool acknowledges VLAIO for Moonshot funding (ARCLATH, nr. HBC.2019.0110, ARCLATH2, nr. HBC.2021.0254).

Effect of surface chemical heterogeneity of carbon textiles on their detoxification activity against CWA surrogate

Marc Florent[1], Paola S. Pauletto[1] and Teresa J. Bandosz[1]

[1]Department of Chemistry & Biochemistry, The City College of New York ,160 Convent Ave, New York, NY 10031 USA
Email for correspondence: tbandosz@ccny.cuny.edu

Activated carbon textiles, owing to their physical form and developed porosity might have a potential to replace activated carbon layers in either gas masks or warfighters' garments. In order to increase their detoxification activity modification of surface chemistry is needed. It is well known that certain functional groups on the carbon surface might increase the catalytic activity [1] and even can provide photoactivity [2], leading to the oxidation of toxic compounds to less toxic species or their decomposition. This heteroatom catalytic activity can be also enhanced by an introduction of an additional active phases [3].

In this work porous carbon textile swatches were first oxidized using various treatments to modify their porosity and to create anchoring sites for an introduction of nitrogen and sulfu -containing functional groups It is interesting that a very strong level of oxidation led to a complete blocking of porosity while preserving a textile morphology and elasticity. NH_3 and H_2S treatments at 500 and 900 ^{o}C were applied to introduce surface groups. The low treatment temperature was expected to functionalize the carbon surface with N and S groups, respectively, and the high one - to dope the heteroatoms to the carbon rings, leading also to a decrease in their surface contents. The samples were characterized by adsorption of nitrogen, thermal analysis, potentiometric titration and XPS.

The decomposition of 2-chloroethyl ethyl sulfide (CEES, > 97% purity), mustard gas surrogate, was tested by dropping 5 μL 2-chloroethyl ethyl sulfide (CEES, > 97% purity), to the center of round-shaped textile samples (0.5-in diameter), which were already placed in hermetically closed glass vessels. The vials were closed and kept in direct light for various periods of time. Then, 2 mL of acetonitrile (> 99% purity) was introduced through the septum and the vial was shaken to extract the species remaining, and weakly bonded, to the surface. The extracts were analyzed by GC-MS.

The results indicated the various levels of catalytic activity which led to the decomposition of CEES to variety of compounds. The level of catalytic activity depended on the strength of CEES interactions with the carbon surface, affected by porosity and hydrophobicity level, on the specificity of groups, and on the absolute amounts of catalytic centers. Overall, the introduction of S and N to the carbon rings increased the speciation of oxidation products/decomposition efficiency, owing to the activation of molecular oxygen by these species

References:

1. M C.O. Ania and T. J. Bandosz. Surface Chemistry of Activated Carbons and its Characterization . In *Activated Carbon Surfaces in Environmental Remediation*, Bandosz, T. J. Ed. pp. 159-230. Elsevier, Oxford, 2006
2. T.J. Bandosz, C.O. Ania. Origin and Perspectives of the Photochemical Activity of Nanoporous Carbons. Advanced Science 2018, 5, 1800293.
3. D. A. Giannakoudakis , T J. Bandosz. Detoxification of Chemical Warfare Agents: From WWI to Multifunctional Nanocomposite Approaches, Springer 2018

Acknowledgements:

This work was supported by US DoD by grant #W911NF2310204.

Adsorption separation of CO2 from CH4/CO2 mixture by Low Silica X zeolite and Recovering of Adsorption Heat for Further Applications

Akihiko Matsumoto[1], Keiichi Hasegawa[1], Yuji Hasegawa[1]

[1] Department. of Applied Chemistry and Life Science, Toyohashi University of Technology,
Tempaku cho,Toyohashi 441-8580, Japan
Email for correspondence: aki@tut.jp

Biogas produced by anaerobic fermentation of sludge contains approximately 60% of methane (CH4), and 40 % of carbon dioxide (CO2) with small impurities. The biogas has been attracting attention as a clean energy because it is carbon neutral unlike fossil fuels. It is important to separate of CO2 from the biogas. The low-silica X zeolite (Na-LSX) is one of useful candidate to the adsorbent because of its strong adsorption ability of CO2 by the strong interaction between the quadrupole of CO2 and the strong electric- field gradient by cation in zeolite cavities. However, the strong interaction brings about high heat evolution which reduces adsorption efficiency. This study focuses on the recovering of the adsorption heat by CO2 adsorption from a model biogas of the CO2- CH4 mixture (CO2/CH4 = 2/3). The laboratory- made heat recovering apparatus in a flow adsorption system is applied to reduce the temperature rise by adsorption. In this apparatus, an adsorption tube containing Na-LSX is placed in a water tank and the heat evolved by CO2 adsorption was efficiently conducted in water. The amount of recovered heat was estimated by the temperature change of water.

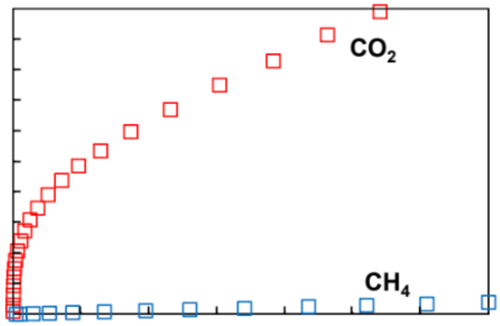


Figure 1 Adsorption isotherms of CO_2 and CH_4 on Na-LSX at 298 K

The adsorption isotherm of CO2 on Na-LSX at 298 K is of type II as shown in Figure 1; the adsorption uptake steely increases by 3 mmol/g at the equilibrium pressure pe of 0.8 kPa and increased linearly till pe = 55 kPa and attained 10 mmol/g. On the other hand, the zeolite scarcely adsorbs CH4. It indicates that CO2 can be successfully separated from the mixed gas by Na-LSX. The differential heat of adsorption of CO2, Qdiff, is 55 kJ/mol at the initial stage of adsorption and gradually decreases with increasing the uptake by 10 mol/g since CO2 adsorption takes place from high energetic sites. In this experiment, about 60 % of adsorption heat is recovered from the temperature change of water and the CO2 uptake estimated by the breakthrough curve.

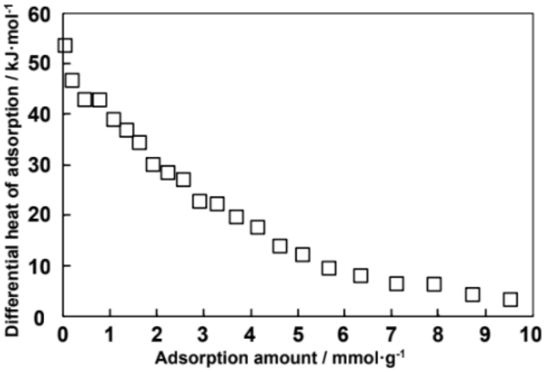


Figure 2 The differential heat of CO_2 adsorption on Na-LSX at 298 K.

Separation Performance of Zeolitic-Imidazolate-Framework-Based Membranes

Michael Tsapatsis[1]

[1] John Hopkins University

Email for correspondence: tsapatsis@jhu.edu

Metal-organic frameworks (MOFs) hold promise as gas separation membranes due to their tunable permeation properties enabled by the structural diversity stemming from the plethora of available metal/organic combinations. Among MOFs, zeolitic imidazolate frameworks (ZIFs) have been studied extensively for their potential as selective separation membranes because their unique structural properties allow them to achieve high performance for certain important separations, like that of propylene from propane. Although relatively rapid progress for highly selective ZIF membranes has been achieved, reliable and scalable thin film processing remains a challenge. In this talk, I will discuss synthesis and post-synthesis modification methods we have been developing based on vapor and liquid phase processing and use of electron-beam-, X-ray- and plasma-induced modifica- tions. These methods may establish a new materials processing paradigm for thin film separation membranes that could allow control of structure, and composition to achieve optimal separation performance.

Unique characterization data of graphene mesosponge

Hirotomo Nishihara[1]

[1] Tohoku University
Email for correspondence: hirotomo.nishihara.b1@tohoku.ac.jp

Graphene MesoSponge® (GMS) is a new type of graphene-based mesoporous material synthesized via template-directed chemical vapor deposition, followed by template removal and high-temperature annealing at 1800 °C1,2. GMS consists mainly of single-layer graphene walls with minimal number of edge sites and enriched topological defects (non-hexagonal carbon rings)3. From its unique structure, the characterization data of GMS are distinct from other porous carbon materials, and it makes us aware of the insight into the interpretation of common characterization techniques used for carbon materials. In this talk, the unique properties of GMS are discussed with its extraordinary characterization data.

X-ray diffraction (XRD) of GMS shows a weak carbon 002 and an intense 10 peaks, indicating not significantly stacked structures and developed graphene domain. Raman spectrum of GMS shows very intense D-band, while exhibiting intense G- and 2D-bands, which are the characteristics of single-graphene structures. Such XRD and Raman data indicate its "non-graphitic" structure, whereas GMS exhibits extraordinaly oxidation resistance even better than single-walled carbon nanotubes (SWCNT)4. Moreover, the electric conductivity of GMS is higher than activated carbons and most of carbon blacks1. Thus, the "low crystallinity" of carbon does not directly related to its chemical stability and conductivity, and XRD and Raman spectroscopy cannot properly evaluate these performances of carbon materials. Is there any good method? Yes, our answer is high-sensitivity temperature-programmed desorption (TPD) up to 1800 °C, which can determine the number of edge sites at a ppm-level in any sp2-based carbon materials. We found that the number of edge sites is directly related to oxidation resistance1 as well as electrochemical stability5,6. Once the number of edge sites is obtained, it is possible to calculate average graphene domain size which is directly related to conductivity of carbon materials.

GMS shows unique elasticity due to its single-graphene walls7, inducing a significant degree of adsorption-induced expansion8. We have developed home-made device which can evaluate adsorption/desorption induced by the application of mechanical force onto mechanically soft nanoporous materials7.

References:

1. H. Nishihara et al., Adv. Funct. Mater. 26, 6418 (2016).
2. S. Sunahiro et al., J. Mater. Chem. A 9 (25), 14296 (2021).
3. W. Yu et al., Adv. Sci. 10, 2300268 (2023).
4. K. Nomura et al., Energy Environ. Sci. 12, 1542 (2019).
5. R. Tang et al., J. Mater. Chem. A 7, 7480 (2019).
6. G. B. Choi et al., Nano Lett. 20, 5885 (2020).
7. K. Nomura et al., Nat. Commun. 10, 2559 (2019).
8. H. Nishihara et al., Carbon Reports 1, 123 (2022).

Formation and Characterization of ZIF-8 Supraparticles and Their Packings with Hierarchical Porosity

Satoshi Watanabe[*1], Atsushi Fujiwara[1], Shotaro Hiraide[1], Minoru T. Miyahara[1], and Nicolas Vogel[2]

[1] Dept. of Chem. Eng., Kyoto University, Katsura, Nishikyo, Kyoto, 615-8510, Japan [2] Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Haberstr. 9a, 91058 Erlangen, Germany
Email for correspondence: nabe@cheme.kyoto-u.ac.jp

Metal–organic frameworks (MOFs) are microporous adsorbents for high-throughput gas separation. Such materials exhibit distinct adsorption characteristics owing to the flexibility of the crystal framework in a nanoparticle, which can be different from its bulk crystal. However, for practical applications, such particles need to be compacted into macroscopic pellets, creating mass-transport limitations. In this work, this problem is addressed by forming materials with structural hierarchy, using a supraparticle-based approach. Spherical supraparticles composed of nanosized MOF particles are fabricated by emulsion templating and they are used as the structural component forming a macroscopic material. Zeolitic imidazolate framework- 8 (ZIF-8) particles are used as a model system and the gas-adsorption kinetics of the hierarchical material are compared with conventional pellets without structural hierarchy. We first synthesized ZIF-8 particles with the size of ca. 200 nm, as building units, using a central collision type microreactor [1] and preparedZIF-8 suspension droplets by mixing an aqueous suspension with an oil phase in a microfluidic device [2], followed by the drying of droplets to form supraparticles. As shown in Fig. 1a, the microfluidic process successfully produced monodisperse supraparticles with a diameter of ca. 40 μm composed of self-assembled nano-sized ZIF-8 particles (Fig. 1b; magnified image of a supraparticle). The calculation of the void fraction of supraparticles based on the ZIF-8 particle concentration, droplet size, and supraparticle size demonstrated that the supraparticles have close-packed structures. Furthermore, it is demonstrated that a pellet packed with supraparticles exhibits a 30 times faster adsorption rate compared to an unstructured ZIF-8 powder pellet.

These results underline the importance of controlling structural hierarchy to maximize the performance of existing materials. In the hierarchical MOFs, large macropores between the supraparticles, smaller macropores between individual ZIF-8 primary particles, and micropores inherent to the ZIF-8 framework collude to combine large surface area, defined adsorption sites, and efficient mass transport to enhance performance [3].

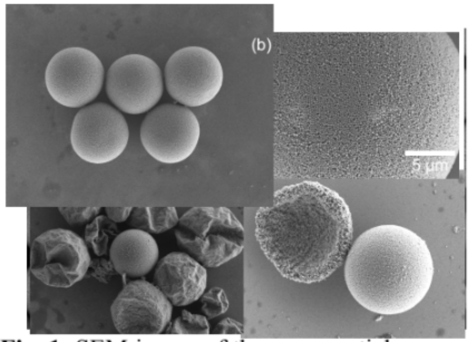


Fig. 1 SEM image of the supraparticles composed of ZIF-8 nanosized particles

References:

1. S. Watanabe, S. Ohsaki, T. Hanafusa, K. Takada, H. Tanaka, K. Mae, M.T. Miyahara, Synthesis of zeolitic imidazolate framework-8 particles of controlled sizes, shapes, and gate adsorption characteristics using a central collision-type microreactor, Chem. Eng. J., 313 (2017) 724-733
2. N. Vogel, S. Utech, G.T. England, T. Shirman, K.R. Phillips, N. Koay, I.B. Burgess, M. Kolle, D.A. Weitz, J. Aizenberg, Color from hierarchy: Diverse optical properties of micron-sized spherical colloidal assemblies, Proc. Natl. Acad. Sci., 112 (2015) 10845-10850
3. A. Fujiwara, J. Wang, S. Hiraide, A. Gotz, M.T. Miyahara, M. Hartmann, B. Apeleo Zubiri, E. Spiecker, N.Vogel, S. Watanabe, Fast Gas-Adsorption Kinetics in Supraparticle-Based MOF Packings with Hierarchical Porosity, Adv. Mater., 35 (2023) e2305980

Functional porous physisorbent materials from phosphorite waste: Advanced characterizations and applications

Ayalew H. Assen[1], Ali Mohammed Yimer[1], Youssef Belmabkhout[1]

[1] Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE), Mohammed VI Polytechnic University (UM6P), Lot 660 - Hay Moulay Rachid, 43150 Ben Guerir, Morocco
Email for correspondence: Ayalew.assen@um6p.ma

Porous materials have sparked tremendous interest as solid sorbents for various applications due to chemical variability and tunability in building blocks, degrees of order, surface areas, pore sizes and shapes, and surface functionalities to optimize their performances. Among the industrially relevant porous physisorbents, zeolites, mesoporous silicas, and metal-organic frameworks (MOFs) have shown promising potential to circumvent the energy and environment-related drawbacks associated with the commonly employed chemical adsorbents. However, their large-scale deployment or widespread adoption is hampered primarily by economic factors related to prohibitively expensive precursors and a lack of green synthesis protocols with industrially feasible steps. Greening the synthetic route for porous materials has piqued researchers' interest as a critical step toward practical industrial applications. In this work, we employed strategic synthesis method to transform the main components of phosphorite waste into different classes of functional porous materials in subsequent steps. The alumina and silica components were isolated to fabricate zeolites and mesoporous silicas while the residual metals were directed to grow MOFs in the subsequent step. The successful assembly of the porous materials was confirmed using various characterization techniques, including XRD, SEM-EDX, TEM, FTIR, TGA-DSC-MS, N_2 adsorption at 77 K, CO_2 adsorption at different temperatures, and H_2O sorption analyses. The resulting zeolites showed enhanced CO_2 capture property. The obtained mesoporous silicas demonstrated to have practical applications for heavy metal capture from wastewater. One of the prepared MOFs with the optimal pore aperture size (~3.4 Å) also showed a potential for alcohol dehydration with a steep and fast moisture adsorption profile and negligible alcohol uptake. Besides recycling waste byproducts, the approach allows the economical production of high-value-added materials that are otherwise expensive to prepare from commercial-grade pure chemicals.

Porous silica-coated magnetic nanoparticles for molecular diagnostics of virus infection

Adriana Zelenakova[1]*, Eva Beňová[2], Nikolas Király[2], Pavol Hrubovčák[1], Jaroslava Szücsová[1], Luboš Nagy[1], Ján Košuth[3], Vladimír Zeleňák[2]

[1]Institute of Physics, P.J. Šafárik University, Park Angelinum 9, 04001 Košice, Slovakia
[2]Institute of Chemistry, P.J. Šafárik University, Moyzesova 11, 04001 Košice, Slovakia
[3]Institute of Biology and Ecology, P.J. Šafárik University, Šrobárova 2, 04154 Košice, Slovakia
Email for correspondence: Adriana.zelenakova@rutgers.edu

Magnetic separation is one of the most efficient and rapid methods currently used for nucleic acid isolation and was used during the COVID-19 pandemic. Magnetic nanoparticles can easily separate viral RNA and DNA from complex clinical samples without the need for centrifugation steps and laborious traditional organic extraction or column separation techniques. Using an external magnetic field, nucleic acids are easily separated and recovered after binding to magnetic nanoparticles. Silica-coated MNPs are widely used to extract biological molecules, including nucleic acids. To increase the yield of nucleic acid separation, MNPs are functionalised by covalently binding various ligands and polymers to their surface, such as amines, aldehydes, polyacrylic acid or APTES (3-aminopropyltriethoxysilane).

At the beginning of the pandemic in 2019, there was a severe shortage of many reagents and consumables, especially RNA isolation kits, required for testing for SARS-CoV-2, due to high demand worldwide. Here, we describe the synthetic procedures for the surface functionalisation of the magnetic core of magnetic nanoparticles to assess their efficacy in isolating viral RNA in diagnostic RT-qPCR. The core is iron oxide Fe3O4 and the shell is a porous layer of silica. The nanoparticle beads were characterised by HRTEM, SEM, FT-IR, XRD and magnetic measurements. The quality of the prepared nanoparticles was verified by isolation of viral RNA from tissue samples infected with hepatitis E virus - HEV and from biofluid samples from SARS-CoV-2 positive patients. The efficiency of RNA isolation was quantified by RT-qPCR. Our results clearly indicate the organisation of a mesoporous structure on the nanoparticle surface. Due to the pores, the specific surface area SBET of amorphous silica has increased to the order of magnitude comparable to the regular mesoporous structures SBA-15 or SBA-16. The potential benefit of this modification is straightforward. The increased surface area provides more silane groups available to bind RNA, improving the efficiency of the particles.

Acknowledgements:

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-20-0512, APVV-SK-SRB-21-0056, No. APVV-20-0072, by the VEGA No. 1/0829/21 and by support from the Team TRIANGEL at the Faculty of Science, P. J. Šafárik University in Košice. This work was also partially supported by the Operational Programme Integrated Infrastructure, project "NANOVIR", ITMS:313011AUW7, co-funded by ERDF. The authors are also grateful to synlab slovakia s.r.o. for support and assistance with SARS-CoV-2 analyses.

CPM9 | POSTER PRESENTATION
CATEGORY: CHARACTERIZATION

Temperature-Dependent V-Type Isotherm Models: Applied to Water Vapor Adsorption on Metal-Organic Frameworks

Cristian Cardenas[1]

[1] IFP Energies Nouvelles
Email for correspondence: cristian.cardenas-sarabia@ifpen.fr

Metal-organic frameworks (MOFs) are highly porous materials with tunable pore characteristics, making them attractive for applications in gas storage, separation, and catalysis [1]. Their unique properties have garnered significant attention in water vapor adsorption technology, crucial for humidity control, air conditioning, and heat pump systems. The Leibniz Supercomputing Center, in collaboration with IBM, has pioneered a water-cooled supercomputer utilizing a water adsorption heat pump (AHP) for efficient waste heat utilization [2].

This study investigates the V-type isotherms displayed by Aluminum-fumarate and CAU-10 MOFs in water vapor adsorption, a phenomenon not extensively studied. Unlike traditional materials like activated carbon, these MOFs exhibit a distinctive "S-shape" adsorption isotherm, indicating a complex adsorption mechanism requiring comprehensive modeling. Existing models, including the Mahle model [3] and Weighted dual-side-Langmuir model [4], while valuable, have limitations in accurately characterizing adsorption behavior, particularly at lower and higher relative pressures.

To address this, we propose a modified Mahle equation tailored for dynamic conditions and temperature- dependent V-type isotherms. Our model extends the range of reliable relative pressures up to 0.8, surpassing the capabilities of established models. Utilizing this model, we conduct dynamic simulations to gain insights into the water vapor adsorption behavior of Aluminum-fumarate and CAU-10 MOFs under diverse conditions.

This study holds significant implications for the advancement of MOF-based heat pump systems, offering a sustainable alternative to traditional refrigerant-based systems. By enhancing our understanding of MOFs' water vapor adsorption properties and developing accurate dynamic simulation models, this research paves the way for more energy-efficient and environmentally friendly heat pump systems. Considering the global drive for sustainable energy solutions, our findings mark a crucial step towards the broader adoption of MOFs in vital applications such as dehumidification, air conditioning, and heat pump systems.

References:
1. X. Chen, H. Gao, Z. Tang, G. Wang, Metal-Organic Framework-based Phase Change Materials for Thermal Energy Storage, Cell Reports Physical Science 1 (2020) 100218. https://doi.org/10.1016/j.xcrp.2020.100218. 2. P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, Characterization of metal-organic frameworks by water adsorption, Microporous and Mesoporous Materials 120 (2009) 325–330. https://doi.org/10.1016/j.micromeso.2008.11.020.
3. J.J. Mahle, An adsorption equilibrium model for Type 5 isotherms, Carbon 40 (2002) 2753–2759.
4. M. Hefti, L. Joss, Z. Bjelobrk, M. Mazzotti, On the potential of phase-change adsorbents for CO2 capture by temperature swing adsorption, Faraday Discuss. 192 (2016) 153–179. https://doi.org/10.1039/c6fd00040a.

Facile Characterization of Pore Accessibility in Metal-Organic Framework/Polymer Composites

Trenton Tovar[1]

[1] U.S. Army, DEVCOM Chemical Biological Center

Email for correspondence trenton.m.tovar.civ@army.mil

Metal-organic framework (MOF)/polymer composites provide the possibility of combining the desired reactive and sorptive properties of highly porous MOFs with the desired mechanical properties of polymers to develop novel functional materials. Both MOF and polymer chemistries are complex leading to various degrees of material compatibility. It is desired to develop a facile measurement of the accessibility of MOF pore space within the composite matrix. Traditionally, N2 isotherms at 77K have been used to characterize pore space in porous materials. We found that using N2 isotherms to assess pore accessibility in MOF/polymer composites underestimates the true value. This is mostly due to the cryogenic temperature of the measurement being below the glass transition temperature of elastomeric polymers. However, composite synthesis and morphology also play a role in the measurement. Measuring CO2 isotherms at 0 °C was shown to be a facile, more accurate measurement of pore accessibility in MOF/polymer composites.

Characterization of hydroxyl groups in zeolite defects using advanced temperature-programmed desorption

Shunsuke Shimizu[1] ,Hirotomo Nishihara [2]; Ryota Osuga [3]; Takeharu Yoshii [2]

[1] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University [2] Tohoku University
[3] Hokkaido University

Emails for correspondence: osuga@cat.hokudai.ac.jp, shunsuke.shimizu.q4@dc.tohoku.ac.jp, takeharu.yoshii.b3@tohoku.ac.jp, hirotomo.nishihara.b1@tohoku.ac.jp

Zeolites are crystalline aluminosilicates that have a wide range of applications, including solid catalysts, adsorbents, and separation membranes. In zeolites, hydroxyl groups exist in various forms, including Brønsted acid sites (BAS), isolated hydroxyl groups, and hydroxyl groups in defects (Fig. 1a). Despite their significant impact on zeolite performance, it has been challenging to quantify and qualify each of them by conventional FT-IR and 1H NMR methods [1,2]. Notably, hydroxyl groups in defects that are hydrogen-bonded to each other exhibit broad bands, making it difficult to assign clear peaks and perform absolute quantification. In this study, we propose employing advanced temperature-programmed desorption (TPD) heating up to 1600 °C under vacuum as a new analytical method to qualitatively and quantitatively analyze hydroxyl groups in zeolite defects. Fig. 1b shows the TPD profile of dealuminated Mordenite (DeAl) in which hydroxyl groups in defects were generated by partly removing aluminum in the original Mordenite. H_2O desorption was observed above 300 °C, and H_2 desorption started at temperatures above 600 °C, with complete elimination of all hydrogen by 1600 °C. The increase in the amount of OH groups due to dealumination determined by TPD was 1882 μmol/g. Considering the amount of Al removal determined by inductively coupled plasma (ICP) analysis, 2.4 hydroxyl groups per one Al defect on average were formed. Combined with the FT-IR results and DFT simulations, we found that pairs of hydroxyl groups forming strong hydrogen bonds in defects desorbed as H_2O, while distant pairs desorbed as H_2 at high temperatures. Therefore, advanced TPD up to 1600°C allows for the qualitative and quantitative determination of hydroxyl groups while discerning hydrogen bond strength, which is difficult with conventional analytical methods.

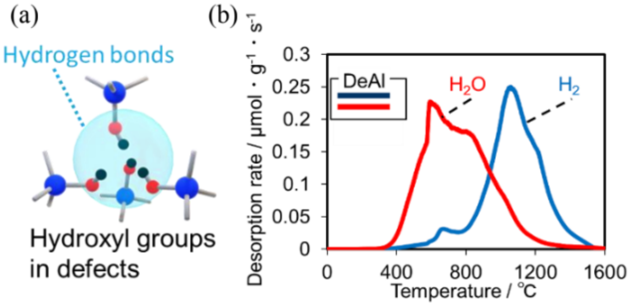


Fig. 1 (a) Hydroxyl groups in defects. (b) TPD profile of DeAl.

References:
1. J. P. Gallas, J. M. Goupil, A. Vimont, J. C. Lavalley, B. Gil, J. P. Gilson, O. Miserque, Quantification of Water and Silanol Species on Various Silicas by Coupling IR Spectroscopy and in-Situ Thermogravimetry, Langmuir, 25 (2009) 5825-5834.
2. E. Dib, I. M. Costa, G. N. Vayssilov, H. A. Aleksandrov, S. Mintova, Complex H-bonded silanol network in zeolites revealed by IR and NMR spectroscopy combined with DFT calculations, Journal of Material Chemistry A, 9 (2021) 27347-27352.

CATEGORY: EXPERIMENTAL METHODS

High sensitivity analysis of nitrogen in carbon materials using temperature-programmed desorption up to 2100 °C

Takeharu Yoshii[1] , Ginga Nishikawa [1]; Hirotomo Nishihara [1]

[1] Tohoku University

Emails for correspondence: ginga.nishikawa@3dc.co.jp, takeharu.yoshii.b3@tohoku.ac.jp,
hirotomo.nishihara.b1@tohoku.ac.jp

Nitrogen-doped (N-doped) carbon materials are attracting attention in various fields, such as catalysis for oxygen reduction reaction. CHN elemental analysis and XPS were conventionally used for analysis of N species, but their measurement accuracy is about 0.1 wt%. Thus, a technique for detailed qualitative and quantitative analysis of N species is desired. Temperature-programmed desorption (TPD) has been popularly used for the analysis of inorganic catalysts and carbon materials. In conventional TPD, a sample is heated to typically around 1000 °C at a fixed heating rate and the desorbed gases are detected for chemical identification as a function of temperature. However, it has not been developed as a quantitative method for an effective determination of the N species, mainly due to the higher thermal stability of N in carbon materials than oxygen. Herein, we pro- pose high-temperature vacuum TPD up to 2100 °C as a new high-sensitivity analytical method for N-doped carbons. In TPD result of N-containing mesoporous carbons, desorption of N-containing gases, NH3, HCN, and N2, was observed in a wide temperature range of 300-1900 °C. The nitrogen content calculated from the total amount of desorbed gas was 7.9 wt%, which is in close agreement to the CHN analysis (8.0 wt%) and XPS analysis (8.5 wt%). Combined with the results of XPS analysis and DFT calculations, we found that the gas emission patterns of NH3, HCN, and N2 obtained by TPD can provide quantitative and qualitative information on the different types of N species including pyrrolic N, pyridinic N, and graphitic N. Furthermore, TPD analysis was performed on a sample with a very small amount of N content and showed a high quantitative accuracy of the order of 10 ppm (0.001 wt%).

CATEGORY: EXPERIMENTAL METHODS

Explorations of the Molecules-to-Materials Continuum

Robert Szilagyi[1]

[1] The University of British Columbia - Okanagan

Email for correspondence: robert.szilagyi@ubc.ca

A continuum in the chemical space linking molecules and materials encompasses promising physical and chemical properties that both extremes do not and cannot display. As we consider transitioning from well-defined structures and compositions toward materials, their surfaces, and grain boundaries through nanoparticles, new chemical reactivity, catalytic properties, and unique chemical functions may hide in plain sight. We have been exploring various continuums established for aluminosilicates [1], iron-sulfur nanoparticles [2], and carbon materials [3], as representative examples for hard, tender, and soft materials, respectively. Our ambitious effort is the bridging of acid/base chemistry of exfoliated clays nanoparticles and Fe-S clusters with rich redox chemistry toward generating organic compounds and materials. Computational molecular cluster models, as maquettes of reactive sites of interest are being employed for studying physisorption on CH₄ and H₂ on carbon surfaces, reactivity of H₂, H₂S, and other small organic molecules with on hybrid Fe-S–clay nanoparticles. The computational work is driving the atomic-level interpretation of spectroscopic features (FTIR, EPR, XANES/EXAFS) and analytical measurements (DTG/DSC-MS). X-ray synchrotron spectroscopy offers the connection between theoretical modeling and experimental work due to mining electronic and geometric structural information for the reactive sites, as a key technique in validating the accuracy of theory and the adequacy of the computational maquettes.

Characterization of Mycelium-Based Leather Using Sorption-Ultrasonic Experiments

Gunel Nabiyeva[1] , Ashoka Karunarathne [2]; Christopher Rasmussen [3]; Naila Assem [3]; Jonathan Bauer [3]; Alexei Khalizov [4]; Gennady Gor [2]

[1] Dept. of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, NJ, USA
[2] Otto H. York Department of Chemical and Materials Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, USA

[3] Bolt Threads Inc., 2261 Market Street Suite 5447, San Francisco, CA 94114, USA

[4] Department of Chemistry and Environmental Science, New Jersey Institute of Technology, 323 Dr. Martin Luther King Jr. Blvd, Newark, NJ 07102, USA

Emails for correspondence: amt74@njit.edu, gn94@njit.edu, khalizov@njit.edu, crasmussen@boltthreads.com, gor@njit.edu

Conventional leather is a product that has been used for millennia. Unfortunately, it suffers from a significant carbon footprint due to its livestock source and tanning (the process of converting hides to leather). In addition, there are ethical issues regarding the consumer use of animal-derived products [1,2]. To mitigate these issues, engineering sustainable bio-based leather substitutes has seen increased interest in material science over the past few years. Among the bio-based materials, mycelium, the fungal "root"of a mushroom, is one of the promising alternatives due to its tunable physico-mechanical properties [2].

Understanding the effect of humidity on leather material properties is essential to tailoring high-quality leather products. To this end, we employed a novel adsorption-ultrasonic measurement technique [3] to investigate the effects of water sorption on the elastic properties of mycelium-based leather materials. The ultrasonic pulse-transmission method was used to measure the wave speed through the materials while simultaneously measuring their adsorption isotherms. The changes in the measured longitudinal modulus during water sorption and evaporation reveal the behavior of the elasticity of the test materials (Fig 1b). Specifically, the observed irreversible change in the longitudinal modulus during the initial branch of water sorption allows to understand better how the material production process and the presence of additives affect the mechanical properties of this bio-based leather material.

References:
1. Ziegler, A. R.; Bajwa, S. G.; Holt, G. A.; McIntyre, G.; Bajwa, D. S. Evaluation of physico-mechanical properties of mycelium reinforced green biocomposites made from cellulosic fibers. Applied engineering in agriculture 2016, 32, 931–938.
2. Fredricks, J. L.; Jimenez, A. M.; Grandgeorge, P.; Meidl, R.; Law, E.; Fan, J.; Roumeli, E. Hierarchi- cal biopolymer-based materials and composites. Journal of Polymer Science 2023, 1–48.
3. Ogbebor, J.; Valenza, J. J.; Ravikovitch, P. I.; Karunarathne, A.; Muraro, G.; Lebedev,M.; Gurevich, B.; Khalizov, A. F.; Gor, G. Y. Ultrasonic Study of Water Adsorbed in Nanoporous Glasses. Phys. Rev. E 108, 2023, 024802.

Validation of pore size distribution from a new GCMC kernel based on a slit-pore model with carbon surface heterogeneity

Author: Kazuyuki Nakai[1]

[1] MicrotracBEL Corp.
Email for correspondence: kazu@microtrac-bel.com

For porous carbons, which typically have hierarchical structures, the pore size distribution (PSD) is one of the most important characteristics and is currently evaluated by using kernel fitting methods represented by non-local density functional theory. Herein, we present new kernels for N2 and

Ar adsorption at 77 K and 87 K, respectively, derived from Monte Carlo (MC) simulations based on a carbon slit-pore model that considers energetic heterogeneity due to surface roughness. The model consists of a locally scaled Lennard–Jones (LJ) 10-4 potential and Steele's 10-4-3 potential, and the scaling factors of the LJ 10-4 potential are assumed to follow a normal distribution that mimics the adsorption behavior on real carbon black. In contrast to our previous MC kernel based on Steele's 10-4-3 potential, the local isotherms of the new kernel did not show a steep increase due to adsorption layer formation. Despite the improved fit for adsorption isotherms, PSDs obtained from the proposed kernel unfortunately show a non-negligible valley around 1 nm, which is a major artifact of the kernel fitting approach. A careful comparison of the smooth and rough surface models indicated that the definitive cause of the artifact lies not in the formation of monolayers, which was believed so far, but rather in the pore-filling behavior, which provides a major clue for constructing a completely artifact-free kernel based on molecular simulations. Finally, the PSDs of four commercial activated carbons were evaluated using the new kernel[3] and compared with our previous GCMC- based kernel[1] and QSDFT[2] in Fig.1.

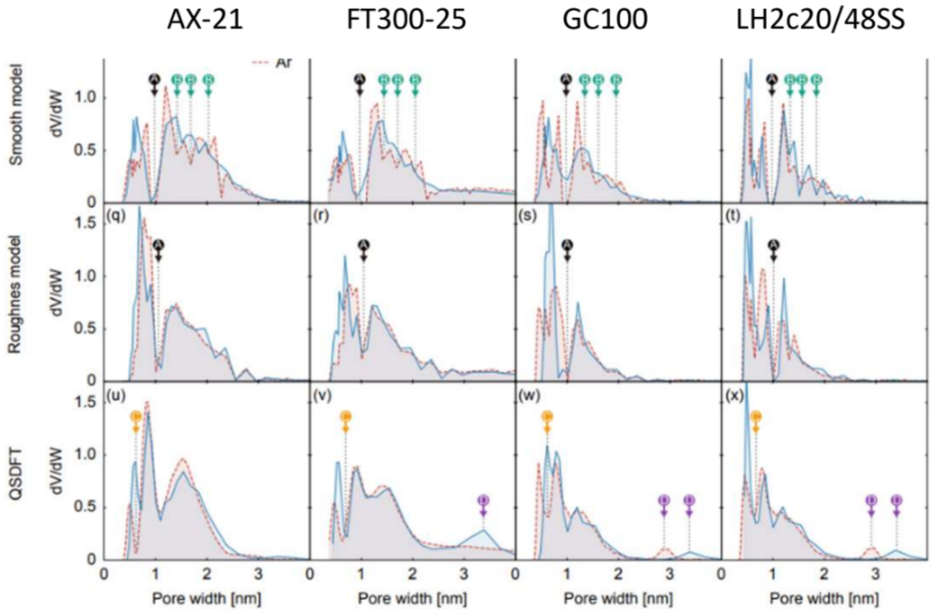


Fig. 1 PSDs of four activated carbons using three different kernels

Kinetics of Adsorption-Induced Deformation in Microporous Materials

Authors: Andrei Kolesnikov[1]; Gennady Gor[2]
[1] Department of Chemical and Materials Engineering, New Jersey Institute of Technology

[2] Princeton University, NJIT
Emails for correspondence: kolesnik@njit.edu, gor@njit.edu

Adsorption of fluids in porous media causes mechanical stress which results in deformation [1,2]. This phenomenon is ubiquitous but challenging to predict quantitatively due to numerous factors (pore size and geometry, adsorbent/adsorbate combination, temperature, etc.) affecting its manifestation. Since many industrial and real-world processes occur far from thermodynamic equilibrium it is important to consider time as one of these factors. In this work, we proposed a kinetic model of adsorption-induced deformation in microporous materials. The model is based on the osmotic potential [3,4], written as a functional of two variables: strain and adsorbate concentration. From the thermodynamic potential, we constructed two differential equations describing the time evolu- tion of the coupled processes - diffusion of adsorbate inside the porous media and the correspond- ing adsorbent deformation. The kinetic equations correspond to conservative and non-conservative cases, respectively. By solving them numerically we calculated spatial concentration and deformation profiles as well as their evolution. We obtained that at sufficiently low strain relaxation rates the deformation process hinders the diffusion, and becomes the limiting one. On the other hand, at high strain relaxation rates, the deformation process is defined by the local adsorbate concentration and "follows" the diffusion. We believe that the proposed model can help in the interpretation of sorption uptakes on microporous materials, including MOFs.

References:

1. G.Y. Gor, P. Huber, N. Bernstein, Adsorption-induced deformation of nanoporous materials—A review, Applied Physics Reviews, 4 (2017) 011303
2. A. L. Kolesnikov, Yu. A. Budkov, G. Y. Gor, Models of adsorption-induced deformation: ordered materials and beyond, 34 (2021) 063002
3. D. Bousquet, F.-X. Coudert, A. G. J. Fossati, A. V. Neimark, A. H. Fuchs, A. Boutin, Adsorption induced transitions in soft porous crystals: An osmotic potential approach to multistability and intermediate structures, The Journal of Chemical Physics, 138 (2013) 174706
4. A. V. Neimark, F.-X. Coudert, A. Boutin, and A. H. Fuchs, Stress-Based Model for the Breathing of Metal-Organic Frameworks, The Journal of Physical Chemistry Letters, 1 (2010) 445.

Sorption-Ultrasonic Characterization of Water-Filled Xerogels

Ashoka Karunarathne[1],Alexei Khalizov [2]; Gennady Gor [3]; Gudrun Reichenauer [4]; Stephan Braxmeier [4]

[1] New Jersey Institute of Technology
[2] Department of Chemistry and Environmental Science, New Jersey Institute of Technology, 323 Dr. Martin Luther

King Jr. Blvd, Newark, NJ 07102, USA
[3] Princeton University, NJIT
[4] Center for Applied Energy Research e.V. (CAE)

Emails for correspondence: gudrun.reichenauer@cae-zerocarbon.de, stephan.braxmeier@cae-zerocarbon.de, amt74@njit.edu, khalizov@njit.edu, gor@njit.edu

Many studies have proven that elastic properties of fluids confined in nanopores deviate from the values observed in bulk [1]. Interactions between the solids (pore wall) and fluids, and pore geometry are the key factors that determine the deviation in the elasticity of nanoconfined fluids. Therefore, experimental measurements of elastic properties of confined fluids can provide information about the porous solids themselves. In this work, we studied the elasticity of carbon xerogels when they are gradually saturated with water. Here, a novel adsorption-ultrasonic experimental setup [2] was employed to measure the ultrasonic wave speeds through the water-saturated carbon xerogel sample while measuring its water sorption isotherm. The measured water sorption isotherm follows type V isotherm [3], which describes the mechanisms of fluid adsorption to the nanopores. Elastic moduli of the xerogel-water composite, derived from the measured ultrasonic wave speeds, were then used to calculate the bulk modulus of the confined water using the Gassmann theory. The resulting elastic properties differ noticeably from those measured on water-saturated Vycor glass [2]. We found that the measured elastic properties of the water saturated carbon xerogels are strongly affected by adsorption-induced deformation [4].

References:
1. C. D. Dobrzanski, B. Gurevich, G. Y. Gor, Elastic properties of confined fluids from molecular modeling to ultrasonic experiments on porous solids, Applied Physics Review 8, 021317 (2021)
2. J. Ogbebor, J. J. Valenza, P. I. Ravikovitch, A. Karunarathne, G. Muraro, M. Lebedev, B. Gurevich, A. F. Khalizov, G. Y. Gor, Ultrasonic study of water adsorbed in nanoporous glasses, Physical Review E 108, 024802 (2023)
3. M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure and Applied Chemistry, 87 (2015) 1051-1069
4. C. Balzer, S. Braxmeier, A. V. Neimark, Gudrun Reichenauer, Deformation of microporous car- bon during adsorption of nitrogen, argon, carbon dioxide, and water studied by in situ dilatometry, Langmuir 2015, 31, 12512–12519

Acknowledgements:
A. K, A. F. K. and G. Y. G. thank the support from NSF CBET-2128679 grant.

Assessment of the Specific Surface Area by Small-Angle X-ray Scattering

Andreas Keilbach[1] , Armin Moser [1]; Heike Ehmann [1]

[1] Anton Paar GmbH

Emails for correspondence: armin.moser@anton-paar.com, andreas.keilbach@anton-paar.com, heike.ehmann@anton- paar.com

The reliable measurement of the specific surface area of many modern materials –porous or non-porous –is of vital importance both in research and industry. To date, the most commonly used method for the determination of the specific surface area of any material is based on the BET (Brunauer-Emmet-Teller) method that relies on the physisorption of gas molecules at the sample surface. The BET method has a number of limitations and challenges, e. g., time-consuming sample preparation/measurement and that the size and effective cross-section of the adsorptive molecules that cover the sample surface is not always known. Small-angle X-ray scattering (SAXS) has good potential to overcome these limitations [1].

In this contribution we will present SAXS as an alternative and complimentary approach for reliable and fast surface area assessment and compare it to the established BET method, showing data for both dense nanoparticle systems as well as highly porous MOF/COF structures.
References:

1. C. Schlumberger, C. Scherdel, M. Kriesten, P. Leicht, A. Keilbach, H. Ehmann, P. Kotnik, G. Reichenauer, M. Thommes, Reliable surface area determination of powders and meso/macroporous materials: Small-angle X-ray scattering and gas physisorption, Microporous and Mesoporous Materials 329 (2022) 111554.

Extruding diffusion constants from your extrudates: PFG-NMR and chromatography

Sean Mclntyre[1] , Daryl Williams [2]; Paola Sáenz-Cavazos [2]; Paul IACOMI [1]

[1] Surface Measurement Systems [2] Imperial College London

Emails for correspondence: paola.saenz-cavazos17@imperial.ac.uk,
smcintyre@surfacemeasurementsystems.com, d.r.williams@imperial.ac.uk,
piacomi@surfacemeasurementsystems.com, dburnett@surfacemeasurementsystems.com

The diffusion of molecules within the confines of a materials pores remains a relatively poorly understood research area. This is despite the diffusion process playing critical role in many adsorption phenomena such as adsorbate selectivity and uptake kinetics. As such, in this work a new model for the analysis of diffusion constants, obtained using a chromatographic Zero-Length Column method, is derived and utilised to accurately determine the micro and macropore diffusion of small molecules in zeolites Na-Y and ZSM-5. In addition to bridging the gap between the NMR and ZLC diffusion analysis techniques.

The proposed mathematical model was derived from the system mass balance, and accounted for fluid-phase contributions, which can be significant in liquid systems[1].

$$\frac{C}{C_0} = \sum \frac{2L - \gamma(\beta_n)^2}{(L - (\gamma(\beta_n)^2)^2 + (\beta_n)^2} e^{-\frac{D\beta_n^2}{R^2}t}$$

Experimental studies of adsorbate desorption from crystals and extrudates of zeolites Na-Y and ZSM-5 were combined with this mathematical model to determine limiting uptake kinetics.

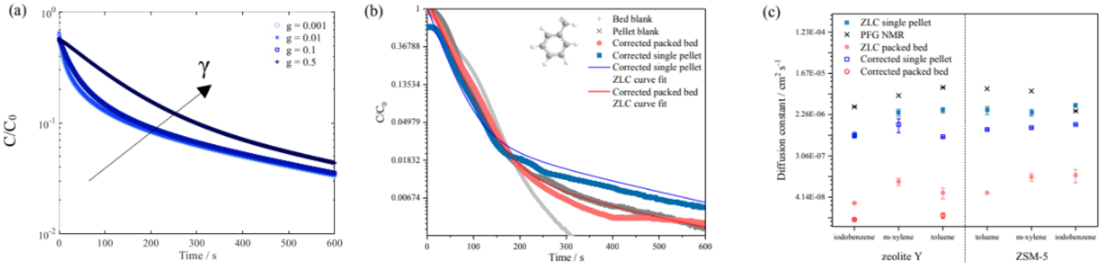


Fig. 1. A) Simulated diffusion curves with increasing fluid-phase hold-up, γ B) Diffusion models fitted to experimental toluene data from zeolite Y C) A comparison of NMR and ZLC diffusion constants.

Diffusion constants were found to increase in extrudate materials, with a larger contribution of macropore diffusion contributing towards the overall diffusion coefficient. This extrudate diffusion was less affected by surface diffusion, resulting in an increased correlation with diffusion constants obtained from Pulsed-Field Gradient NMR when compared to those obtained from more crystalline samples.

References:

1. Sean R. McIntyre, Elwin Hunter-Sellars, Paola A. Sáenz-Cavazos, Anthony R. Houghton, Daryl R. Williams, Novel zero-length column analysis of desorption curves for single cylindrical pellets, Powder Technology, 416, (2023), 118207.

Acknowledgements:

Thank you to the EPRC and Imperial College London Departmental Scholarship.

Impact of Crystal Structure on Methanol Vapor Adsorption in MFI-Type Zeolites: Equilibrium Isotherms and Kinetic Insights

Coset Abreu Jauregui[1] ; Francisco Murilo Tavares de Luna[2] ; Igor de Mesquita Figueredo[2] ; Joaquín Silvestre- Albero[1]; Leandro Martins[3]

[1] University of Alicante
[2] Universidade Federal do Ceará [3] Universidade Estadual Paulista

Emails for correspondence: muriloluna.ufc@gmail.com, joaquin.silvestre@ua.es, coset.abreu@ua.es

Porous materials stand at the forefront of adsorption research, offering versatile applications in separation processes and catalysis for both fundamental research and industrial purposes. Among the numerous applications, methanol separation through adsorption mechanisms is an interesting topic due to the high-value accessible derivatives (purified methanol, hydrocarbons, olefins). Therefore, as a first approach, this study focused on the adsorption behavior of methanol vapor on synthesized MFI-type zeolites. Through a meticulous characterization process, including ill-crystalized (IC), fully crystalized (FC), and hierarchical (HZ) zeolites, we aimed to unveil the influence of material properties on methanol adsorption capacity and accessibility. Equilibrium adsorption experiments conducted at 313.15 K provided critical insights by elucidating the distinctive adsorption behavior across the zeolite samples. The observed isotherm pattern was accurately fitted with the Dubinin–Astakhov model. Notably, the synthesized zeolites exhibited varying adsorption capacities, with hierarchical structures demonstrating superior methanol adsorption over fully and ill-crystalized counterparts, which was also confirmed by calorimetry immersion analysis. Furthermore, our investigation fo- cused on the kinetics of the methanol accessibility within MFI-type zeolites, employing three mod- els: Elovich, Weber-Morris, and Boyd. Estimation of kinetic parameters allowed for a comprehensive evaluation of the adsorption behavior at different loading conditions. The findings showcased dis- tinct kinetic behavior and exposed the influence of material composition on the adsorption kinetics, finally elucidating the methanol-vapor interaction with MFI-type zeolites. Overall, there is an evi- dent and intricate interplay between material chemical properties, adsorption capacity, and vapor accessibility. These insights emphasize the prospect of customizing materials to optimize their per- formance in diverse adsorption applications.

References:

1. M. Thommes, R. Guillet-Nicolas, K.A. Cychosz, Physical Adsorption Characterization of Mesoporous Zeolites, in: Mesoporous Zeolites, John Wiley & Sons, Ltd, 2015 p.349–384.
2. F. Bisinella Scheufele, A. Nivaldo Módenes, C.E. Borba, C. Ribeiro, F.R. Espinoza-Quiñones, R. Bergamasco, N. Curvelo Pereira, Monolayer–multilayer adsorption phenomenological model: Kinetics, equilibrium and thermodynamics, Chemical Engineering Journal, 284 (2016) 1328-1341.
3. P.Y. Ramos Suzaki, M. Tombini Munaro, C. Contini Triques, S. Jaiana Kleinübing, M.R. Fagundes Klen, L.M. de Matos Jorge, R. Bergamasco, Biosorption of binary heavy metal systems: Phenomenological mathematical modeling, Chemical Engineering Journal, 313 (2017) 364-373.

Acknowledgements:
Authors acknowledge financial support from MINECO (PID2019-108453GB-C21), MCIN/AEI/10.13039/ 501100011033, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and EU “NextGeneration/PRTR (Project PCI2020-111968/ERANET-M/3D-Photocat, Maria Zambrano-08).

Quantification of Copolymer Microstructure from Liquid Chromatography using a Statistical Interaction Model

Christopher Rasmussen[1]; Yefim Brun[2]

[1] Bolt Threads Inc.
[2] International Flavors and Fragrances

Emails for correspondence: crasmussen@boltthreads.com, yefim.brun@iff.com

Copolymers have a microstructure defined by their constituent monomers' sequence. This microstructure can have a wide-ranging impact on its structure-function properties and is often difficult to control during polymerization, thus is crucial to understand. Quantification of synthetic copolymer microstructure is challenging due to the large heterogeneity of molecular species and the limited classes of analytical instrumentation available to study high molecular weight molecules. Polymer chromatography is an attractive technique due to its ability to capture distributed properties, and tune separation selectivity for molecular weight (i.e. chain length) or monomer chemistry. It is per- formed using the broad tools of high-performance liquid chromatography (HPLC), but with careful attention paid to the thermodynamics of the polymer-solvent-porous substrate interaction. The most common application of polymer chromatography is size exclusion chromatography (SEC), where enthalpic interactions are minimized and the resulting separation is driven by the entropic tendency of large molecules to avoid small pores. This results in a separation by solute size and is the standard approach to quantify a polymer's molecular weight distribution.

Other experimental situations are possible. For example, if a solvent-substrate pair is selected to approximately balance entropic exclusion and enthalpic adsorption, the retention effects of chain length can be muted. This phenomenon is called the critical point of adsorption (CPA) and has been shown to be sensitive to copolymer composition and microstructure [1]. The elution of polymers can be modelled in these conditions with a relatively simple interaction model [2], which was extended numerically to more complex polymers [3]. This work further extends these approaches to a real-world characterization problem: assessing and monitoring the transesterification of a novel polyester with PET. This was accomplished by including a Markov Chain model to describe the copolymer microstructure [4] and development of suitable chromatographic and spectrographic conditions. We show that the degree of transesterification can be quickly and accurately assessed using these methods. Further, we show how this approach is applicable to any copolymer system that elutes at a CPA.

References:

1. Y. Brun; C.J. Rasmussen. Chapter 11 –Interaction Polymer Chromatography. In: S. Fanali, P.R. Haddad, C.F. Poole, M.-L. Riekkola, editors. Liquid Chromatography (Second Edition); Elsevier, 2017 p. 275–318.
2. Y. Brun; Peggy Foster. Characterization of synthetic copolymers by interaction polymer chromatography: Separation by microstructure; J. of Separation Science, 33 (2010) 3501–3510.

3. C.J. Rasmussen. Molecular Simulation of Simple Fluids and Polymers in Nanoconfinement. Doctoral dissertation, Rutgers, The State University of New Jersey. ProQuest Dissertations Publishing, 2012.
4. F.P. Price. Copolymerization Mathematics and the Description of Stereoregular Polymers; J. Chem. Phys., 36 (1962) 209–218.

Estimation of porous media transport properties solely based on mercury intrusion porosimetry

David Grégoire[1] , Gilles Pijaudier-Cabot [1]; Fadi Khaddour [1]; Lionel Ecay [1]; Sara Khalil [1]

[1] Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France Corresponding

Email for correspondence: david.gregoire@univ-pau.fr

The relationship between the microstructure of porous media and their permeation properties is a problem that has been addressed in many instances. Experimental measurement of intrinsic permeability remains a challenge, especially for tight materials, and several approaches have been proposed in the literature to directly compute the transport property of a porous medium (e.g. network models or continuous-based upscaling). If these techniques can now be very powerful, they remain quite computationally demanding. Other approaches, used widely in engineering applications, rely on analytical formulas in which the input is the characterization of the pore size distribution (PSD) of the material. Pioneering works by Kozeny (1927) have been followed by various approaches where the PSD is first simplified, averaged or idealized to estimate the transport properties. However, these simplifications can lead to important error in the final transport property estimation, especially for tight material.

This contribution presents a model capable of providing estimates of the transport properties directly from the pore-size distribution without any idealization. The model is based on a hierarchical assembly of capillaries with decreasing diameter, generated randomly. The technique yields a porous network, which mimics the pore space measured experimentally by mercury intrusion. The intrinsic permeability and the evolution of the apparent permeability with mean pressure are provided by equating Darcy's law and a combination of Poiseuille's and Knudsen's laws [1]. Gas and liquid relative permeabilities can be also derived [2]. The technique has the advantage of remaining simple and engineering-oriented while allowing accurate estimation over several orders of magnitude of permeabilities (from 10-19 to 10-12) for very different kind of porous materials (see Figure 1). During the conference, new measurements will be presented and discussed on various synthetic and natural materials.

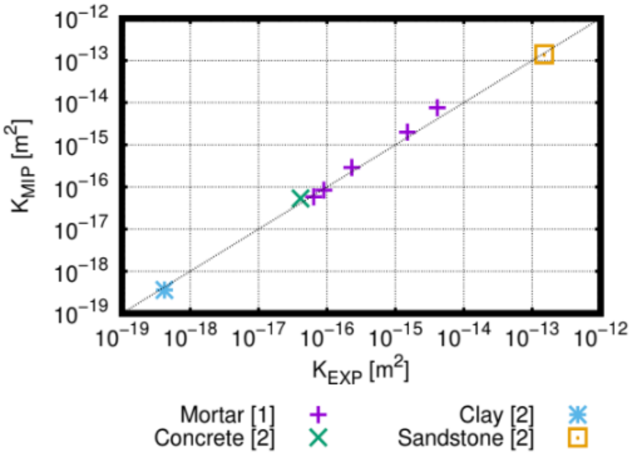


Figure 1. Comparison between different intrinsic permeabilities experimentally measured and estimated based on mercury intrusion porosimetry for different materials.

The influence of confinement effects on the thermophysical properties of 4-methoxyazobenzene

Timm Kraus[1] ,Michael Fröba [1]

[1] Universität Hamburg
Emails for correspondence: michael.froeba@uni-hamburg.de, timm.kraus@uni-hamburg.de

Due to global warming and the high global demand for energy, the research and development of sustainable energy storage systems is of great interest. The photoswitchable phase change material 4-methoxy- azobenzene (4-MeO-Azo) allows simultaneous storage of two different forms of energy which can be released after an external trigger, shown in Fig. [1]. Herein, we report the change of the thermophysical properties of 4-MeO-Azo in confinement. Mesoporous silica like SBA-15, KIT-6 and SBA-16 were impregnated with 4-MeO-Azo to investigate the influence of different pore sizes and pore shapes on the melting point of trans-4-MeO-Azo by differential scanning calorimetry (DSC). The porous materials were impregnated with a load of 120 % of the theoretical pore volume measured by N2-physisorption. The overload was used for internal signal calibration. So far, no crystallization of the cis-isomer has been detected, but only a glass transition, which was not investigated due to its weakness. In addition, the composites were irradiated for one hour with UV light (365 nm) to initiate trans to cis isomerization. This was followed by DSC measurement to investigate the dependence of the thermally induced cis to trans reaction on confinement. The integral of the exothermic signal enables the calculation of the conversion ratio. We were able to infer the following trends: (i) the melting point of trans-4-MeO-Azo decreases with decreasing pore size, (ii) the higher the mean curvature of the pores - from cylindrical (SBA-15) to curved cylindrical (KIT-6) to spherical (SBA-16) with same pore width - the lower the melting point, a trend that can be explained by the Gibbs-Thomson form factor, and (iii) the conversion ratio of the light-induced trans to cis conversion at r.t. seems to be higher in confined space compared to 4-MeO-Azo in bulk, whereas the heat-induced back reaction seems to be unaffected by the confinement.

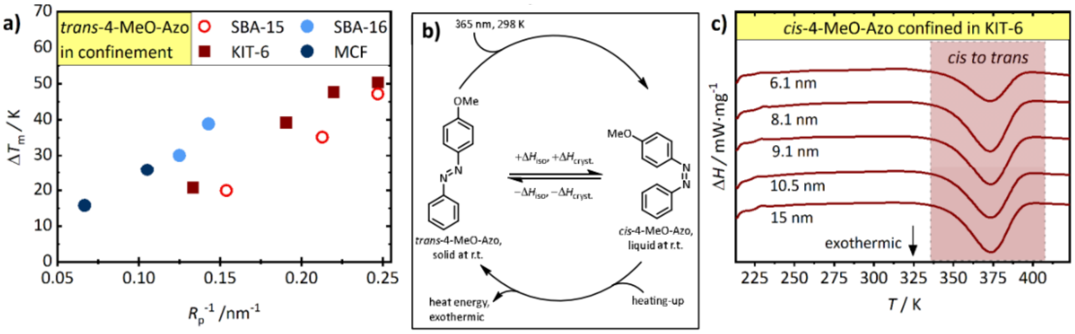


Fig. 1: a) Melting points $T_{\max}$, b) Storage cycle of 4-MeO-Azo, c) DSC-measurement after irradiation.

References:

1. Z. Zhang, Y. He, Z. Wang, J. Xu, M. Xie, P. Tao, D. Ji, K. Moth-Poulsen, T. Li, Photochemical Phase Transitions Enable Coharvesting of Photon Energy and Ambient Heat for Energetic Molecular Solar Thermal Batteries That Upgrade Thermal Energy, J. Am. Chem. Soc., 142 (2020) 12256-12264.

CPM9 | POSTER PRESENTATION
CATEGORY: DATA / AI / ML

PyCOSMOS: A Python Tool for Compartmentalization of Unit Cells of Metal-Organic Frameworks

Shivam Parashar[1] , Alexander Neimark [1]

[1] Department of Chemical and Biochemical Engineering, Rutgers University, New Jersey, USA

Emails for correspondence: sp1709@soe.rutgers.edu, aneimark@rutgers.edu

Metal-Organic Frameworks (MOFs) stand out as a prominent class of nanoporous materials, known for their stability and customizable pore sizes and chemistry, particularly for gas storage and separations. Notably, certain MOFs exhibit pH sensitivity, rendering them excellent candidates for drug delivery applications. The precise characterization of MOFs is of paramount importance for effective design and synthesis for a given application.

Real MOF samples often deviate from ideal crystals due to presence of binders, residual solvents, and pore blockage defects. To characterize this non-ideality at the pore level, we recently introduced the method of calculating pore accessibilities by comparing the in silico calculated fingerprint isotherms and experimental isotherms.1 However, accurate calculation of fingerprint requires knowledge of the shape, size and location of the pore which can be difficult to deduce from the structure alone. In this work, we developed a python program, pyCOSMOS, to describe the shape, size, and location of the pores of MOFs.2 Using the pore size distribution probe particles as input, a special cluster- ing algorithm identifies the pores of different types. Later, the unit cell is decomposed into pore compartments, and Monte Carlo simulations of gas adsorption are performed for calculating the fingerprint isotherms. The generalizability of the program is demonstrated by application to most practical MOFs like Cu-BTC, IRMOF-1, UiO-66, PCN-224, ZIF-412, as well as various structures from the CoRE MOF database.

Acknowledgements:

This work is supported by the NSF CBET grant 1834339.

References:
1. Parashar, S.; Zhu, Q.; Dantas, S.; Neimark, A. V., Monte Carlo Simulations of Nanopore Compartmentalization Yield Fingerprint Adsorption Isotherms as a Rationale for Advanced Structure Characterization of Metal–Organic Frameworks. ACS Applied Nano Materials 2021, 4 (5), 5531-5540.
2. Parashar, S; Neimark, A.V.; Pore Structure Compartmentalization for Advanced Characterization of Metal-Organic Framework Materials. Theo. & Comp. Chem. ChemRxiv. 2023.

Modelling Kerogen Flexibility in Response to Hydrocarbon Adsorption using Hybrid Molecular Dynamics/Monte Carlo

Shivam Parashar[1] , Alexander Neimark [1], Peter I. Ravikovitch [2]

[1] Department of Chemical and Biochemical Engineering, Rutgers University, New Jersey, USA

[2] ExxonMobil Research and Engineering Company

Emails for correspondence: peter.ravikovitch@exxonmobil.com, sp1709@soe.rutgers.edu, aneimark@rutgers.edu

Shale gas reservoirs plays a pivotal role in natural gas production in the United States. Organic part of shale is both a source and reservoir of hydrocarbons. Kerogen, an insoluble organic part of shale, exhibits an amorphous structure, and its composition and mechanical properties depend on the level of maturity. It has been shown the kerogen matrix swells upon gas adsorption. It is critical to understand the structure and adsorption characteristics of organic porosity found in kerogen. This knowledge is crucial for predicting the storage capacities of oil and gas, as well as enhancing hydrocarbon recovery.

To begin, we create three-dimensional molecular models of microporous kerogen matrix of type II-A with the same density and pore size distribution as an experimental sample. We also create slit pores of different sizes using the equilibrated kerogen matrix.1 We study adsorption of CH4, CO2, and octane in flexible kerogen matrix and slit pores. To incorporate the effect of adsorption stress exerted by the gas molecules on kerogen matrix, we use the hybrid molecular dynamics/Monte Carlo approach. This involves multiple cycles of grand canonical Monte Carlo simulations and molecular dynamics in NPT ensemble until the convergence in the number of particles and unit cell volume is achieved. Through our hybrid approach, the study aims to gain a deep understanding of deformation of kerogen upon hydrocarbon adsorption. This holds significant implications for advancing techniques for hydrocarbon recovery from shale reservoirs.

Acknowledgements:

This work is supported by the NSF CBET grant 1834339 and ExxonMobil.

References:
1. Parashar, S; Ravikovitch P.I.; Neimark, A.V. Molecular Modeling and Adsorption Characterization of Micro-Mesoporous Kerogen Nanostructures. Energy & Fuels. 2022.

Characterization of Nanoporous Carbons Using Generative Models

Lucas J. Santos[1]; Elvis do A. Soares[1]; Amaro Gomes Barreto Jr.[1]; Frederico Wanderley Tavares[1]

[1] Universidade Federal do Rio de Janeiro
Emails for correspondence: elvis.asoares@gmail.com, lucasjs@eq.ufrj.br, amaro@eq.ufrj.br, tavares@eq.ufrj.br

Traditional methods of characterization of nanoporous carbons are based on the use of a simulated kernel of isotherms obtained by classical density functional theory (cDFT) in a series of independent slit or cylindrical pore models to compute the pore size distribution. This approach cannot describe the structure's asymmetry, a feature characteristic of these materials. Vallejos et al. [1] used 3D carbon structure models to generate kernels in recent work. They found relative contributions of these structures in experimental isotherms, calculating morphological parameters of the experimental sample and plausible simulated (Transmission Electron Microscopy) TEM images. In this work, we try to predict molecular structures of real materials from a set of experimental data (adsorption properties and images from TEM) using score-based diffusion models. The score-based diffusion model is a deep generative model that has achieved state-of-the-art sample quality in several tasks, including image generation by Computed Tomography (CT) and Magnetic Resonance Imaging (MRI). In this approach, we perturb data with a sequence of noise distributions and generate samples by learning to reverse this path from noise to data. The framework of score-based diffusion models involves gradually diffusing the data distribution towards a given noise distribution using a stochastic differential equation (SDE) and learning the time reversal of this SDE for sample generation. Crucially, the reverse-time SDE has a closed-form expression that depends solely on a time-dependent gradient field, called the score, of the perturbed data distribution. This gradient field can be efficiently estimated by training a neural network from a score-based model with a weighted combination of score-matching losses as the objective. The coupling of adsorption properties and images from TEM with score-based generative models to solve the inverse problems related to the reconstruction of the porous material structure has enormous potential for broadly impacting the porous material characterization area.

References:
1. F. Vallejos-Burgos, C. de Tomas, N. J. Corrente, K. Urita, S. Wang, C. Urita, I. Moriguchi et al. 3D nanostructure prediction of porous carbons via gas adsorption. Carbon, 215 (2023) 118431
2. Y. Song, C. Durkan, I. Murray, S. Ermon. Maximum likelihood training of score-based diffusion models. Advances in Neural Information Processing Systems, 34 (2021) 1415-1428
3. Y. Song, L. Shen, L. Xing, S. Ermon. Solving inverse problems in medical imaging with score-based generative models. arXiv preprint arXiv:2111.08005 (2021)
4. Y. Song, J. Sohl-Dickstein, D. P. Kingma, A. Kumar, S. Ermon, B. Poole. Score-based generative modeling through stochastic differential equations. arXiv preprint arXiv:2011.13456 (2020).

Acknowledgments:
The authors thank Petrobras and Shell, which provided financial support through the Research, Development, and Innovation Investment Clause in collaboration with the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP, Brazil). Additionally, this research was partially funded by CNPq, CAPES, and FAPERJ.

CPM9 | POSTER PRESENTATION
CATEGORY: EXPERIMENTAL METHODS

A Novel Method for Obtaining Carbon Molecular Sieves for N2/O2 Separation

Koki Urita[1] ,Kaito Marubayashi [1]; Miyu Hamasaki [1]; Hideki Tanaka [2]; Takashi Ishida [3]; Yasuyuki Yamane [3]; Jin Miyawaki [4]; HIroo Notohara [1]; Isamu Moriguchi [1]

[1] Nagasaki University [2] Shinshu University [3] OGC
[4] Kyushu University

Email for correspondence: urita@nagasaki-u.ac.jp

The use of oxygen-enriched air with high oxygen concentration is expected to reduce fuel consumption in industrial furnaces. The pressure swing adsorption method was used for the air separation. However, temperature swing adsorption (TSA) using combustion exhaust heat is expected to save more energy. To achieve highly efficient air separation by introducing TSA, a molecular sieve adsorbent whose pore entrance diameter is optimized for preferential adsorption of oxygen is required [1]. Because the electrochemical oxidation (ECO) process adds oxygen-containing functional groups (OCFGs) to carbon materials [2], ECO can be expected to narrow the pore entrance. ECO is usually performed using block carbon electrodes obtained by mixing with a binder. On the other hand, a flow-type ECO is operated by pumping the suspension into the electric field using a suspension of the electrolyte and carbon materials. In this study, we examined the conditions for the addition of OCFG to porous carbons by flow-type ECO and aimed to create a molecular sieving carbon with oxygen/nitrogen selectivity. XPS analysis indicated that the oxygen content on the carbon surface was increased by ECO, and the addition of OCFGs to the porous carbon surface is possible in the flow-type ECO method even though the carbon electrode is not fixed on a current collector. Oxy- gen adsorption isotherms at 20 °C and 80 °C showed that effective oxygen adsorption was decreased in the ECO-treated samples. The decrease in the adsorbed amount should stem from partial pore occlusion and pore size reduction by the addition of OCFGs to the pores. However, by compar- ing the adsorption time required to reach the adsorbed amount to half the equilibrium adsorption amount before and after ECO treatment, it was found that the adsorption rate of nitrogen was significantly reduced by the ECO treatment. These results suggest that the addition of OCFGs to the pore entrance of porous carbon by ECO is effective for the fabrication of carbon molecular sieves for oxygen/nitrogen separation.

INFRAsorp & MULTIport Rapid surface analysis by optical calorimetry

Stefan Kaskel[1] , Felix Spranger [2]
[1] Fraunhofer IWS; TU Dresden

[2] Fraunhofer IWS
Emails for correspondence: stefan.kaskel@iws.fraunhofer.de, felix.spranger@iws.fraunhofer.de

The assessment of specific surface area and adsorption properties in advanced functional materials is a key task for the characterization of porous materials such as activated carbons, porous polymers, metal-organic frameworks, zeolites, nanoparticles and catalysts. The characterization of porous materials by nitrogen Physisorption at 77 K and gravimetric methods is widely used. However, a major drawback of the methods is that a significant amount of time is required for a single experiment. Especially in time critical applications like delivery- or production control or for material screening applications, a fast characterization method would be desirable.

For this particular application, we introduce the approach of optical adsorption calorimetry. It measures the time-resolved temperature change (thermal response) of a porous sample, which occurs during adsorption of a test gas due to the release of heat of adsorption [1,2]. The magnitude of temperature change depends on the heat capacity of the material, the number of adsorbed molecules; the amount of heat released by each molecule, the speed of adsorption as well the heat transfer properties (convection, conduction, radiation) within the sample and the optical calorimeter.

The INFRAsorp is the optical calorimeter tool for a high throughput adsorption screening, developed by Fraunhofer IWS. Additionally, the advanced MULTIport device is available. It enables automatic measurements of up to 12 samples and different adsorptives. It is suited for various test gases like n-butane, VOCs, CO2, H2S and H2O among others [3]. Other advantages of the technique are the small sample size (< 30 mg), that no cooling or liquid nitrogen is required due to measurement at 298 K and the small footprint and compact design of the device.

References

[1] P. Wollmann, M. Leistner, U. Stoeck, R. Grünker, K. Gedrich, N. Klein, O. Throl, W. Grählert, I. Senkovska, F. Dreisbach and S. Kaskel, “High-throughput screening: speeding up porous materials discovery,”Chemical communications (Cambridge, England), vol. 47, no. 18, pp. 5151-5153, 2011. [2] P. Wollmann, M. Leistner, W. Grählert, O. Throl, F. Dreisbach and S. Kaskel, “Infrasorb: Optical detection of the heat of adsorption for high throughput adsorption screening of porous solids,”Microporous and Mesoporous Materials, vol. 149, no. 1, pp. 86-94, 2012.
[3] M. Wöllner, N. Klein and S. Kaskel, “Measuring water adsorption processes of metal-organic frameworks for heat pump applications via optical calorimetry,”Microporous and Mesoporous Materials, vol. 278, pp. 206-211, 2019.

Unique dissolution/precipitation phenomena in microspace induced by physisorption

Takeru Yokoyama[1]; Taku Iiyama[2]; Ryusuke Futamura[2]; Takahiro Ueda[3]; Yuka Matsuda[4]

[1] Faculty of Science, Shinshu University 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan [2] Shinshu University
[3] Osaka Universty
[4] Osaka gas chemical

Emails for correspondence: 22ss315a@shinshu-u.ac.jp, ueda@chem.sci.osaka-u.ac.jp, ryu_f@shinshu-u.ac.jp

In this study, we used mesoporous silica MCM-41 as the vessel of the micro-solution, dibenzyl as solute, and water and diethyl ether as solvents. The water adsorption isotherm of dibenzyl pre-adsorbed MCM-41 (MCM-Dib) shows a new type of isotherm shape which not classified by IUPAC. The water adsorption amount is independent of the amount of dibenzyl (φ_Dib) and agreed with the pore capacity of a raw MCM-41. We confirmed by DSC, wide-angle X-ray scattering and NMR measurement that the precipitation of dibenzyl occurs outside of the pores at second step of the water isotherm. In this micro-solution system, opposite to the bulk, the solute precipitates as the amount of solvent increases. In the case of diethyl ether, the adsorption amount increased specifically at high relative pressure, reaching 3.5 times that of a raw porous solid. This increase in adsorption is attributed to the formation of the new solution phase on the outside of the pores. These results indicate that the combination of dibenzyl and water, which is insoluble in the bulk, is soluble in the pore. The micro-solution formed in the pores is promising as a new reaction field, and their unique reverse dissolution and precipitation behavior is expected to be used for drug delivery and other applications.

Reference Isotherms for Water Vapor Sorption on Nanoporous Carbon: Results of an Interlaboratory Study

Huong Giang Nguyen[1]; Blaza Toman[1]; Roger van Zee[1]; Matthias Thommes[2]

[1] National Institute of Standards and Technology
[2] Friedrich-Alexander-University Erlangen-Nürnberg

Emails for correspondence: huong.nguyen@nist.gov, roger.vanzee@nist.gov, blaza.toman@nist.gov

The ubiquitous nature of water makes understanding its effects on the chemical structure and proper- ties of materials important to the development, processing, and applications of materials associated with food production, pharmaceuticals, construction, separation processes, sorbent-based industries, and emerging water sorption applications such as water harvesting and thermal energy storage.

A water vapor sorption isotherm is a measure of water content as a function of relative pressure (P/P0) for pure water measurements or relative humidity (RH), when water is entrained in another gas. With the large number of isotherms generated by automated instrumentation, there is an increasing need for standardized measurement protocols, reference materials, and reference data. The National Institute of Standards and Technology (NIST) initiated a program to develop reference mate- rials, reference data, and measurement protocols to improve adsorption metrology. The NIST Facility for Adsorbent Characterization and Testing (FACT Lab) recently led an interlaboratory study (ILS) to develop reference water vapor isotherms.

This ILS, sponsored by the Versailles Project on Advanced Materials and Standards (VAMAS), investigated water vapor sorption on a pelletized nanoporous carbon at 25 °C as a function of relative pressure (P/P0) for pure water measurements and relative humidity, when a carrier gas is used. The sorbent used in this study is a certified reference material (CRM) with a high BET specific surface area produced by the German Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und prüfung or BAM) and is known as BAM-P109. This study examines both static and dynamic measurements at sub-atmospheric and atmospheric pressures, because the saturation pressure of water at 25 °C is only 3.17 kPa. This study is the first ILS to report reference data for a vapor sorption isotherm using a CRM. Thirteen laboratories participated in the study and contributed nine pure water vapor isotherms and four relative humidity isotherms, using nitrogen as the carrier gas. From these data, were reference isotherms, along with the 95% uncertainty interval (Uk=2), were determined and are reported.

Small-angle neutron scattering reveals high-density adsorbed hydrogen in carbon micropores at low pressures and supercritical temperature

Sebastian Stock[1], Malina Seyffertitz ; Nikolaos Kostoglou ; Max Valentin Rauscher ; Bruno Demé ;
Christian Mitterer; Osakr Paris

[1] Montanuniversität Leoben, Chair of Physics

Emails for correspondence: christian.mitterer@unileoben.ac.at, max.rauscher@unileoben.ac.at,
sebastian.stock@unileoben.ac.at, nikolaos.kostoglou@unileoben.ac.at, deme@ill.fr,
malina.seyffertitz@unileoben.ac.at, oskar.paris@unileoben.ac.at

This study reports on the low-pressure supercritical Hydrogen (H2) and Deuterium (D2) adsorption in a nanoporous activated carbon cloth, investigated by small-angle neutron scattering (SANS) to elucidate pore size dependent adsorbate densification [1]. The changes of the SANS signal resulting from the physisorption of adsorbate molecules in the pore space are described by analytical pore scattering functions resembling slit-like pores. Based on a hierarchical pore model, we are able to quantify the pore-size-dependent physical density of the confined gas for three pore classes, resembling roughly the IUPAC classes of ultramicropores, supermicropores, and mesopores. Within the very smallest pores, we find the adsorbate density of both, H2 and D2, approaching the bulk solid density of the adsorbate for pressures of about 1 bar at 77 K, while the adsorbate density remains much lower for larger pores. The implications of these results for the design of optimized carbons for low pressure / high temperature hydrogen adsorption are discussed. Moreover, the limitations of the approach and possible ways of overcoming them are also critically reviewed.

Scalable Continuous Flow Hydrogenation Using Structured Catalyst Reactor

Authors: Andrea Adamo[1]; James Mannino[2]; John Holcombe[2]; Lorenzo Milani[1]; Steve Stark[2]; Vladimiros Nikolakis[2]
[1] Zaiput Flow Technologies

[2] W.L. Gore & Associates Inc.
Email for correspondence: vnikolak@wlgore.com

In this talk we present a scalable solution for continuous heterogeneous catalysis, such as hydrogenation reactions. First, we discuss the Gore Structured Catalyst, a 3-dimensional PTFE mesh-based structure embedded with particles of supported catalyst. This 3-dimensional structure has tunable properties, such as porosity and catalyst loading, thus allowing for the construction of a structure with good catalyst mass loading at a low resistance to flow. We discuss then a new modular and scalable reactor design conceived to take full advantage of the Structured Catalyst substrates. We present design principles, scalability arguments, and experimental results with a model hydrogenation reaction. This case study highlights high catalyst utilization, tight temperature control, operation under high pressure, moderate pressure drop, quick scalability of the process, and no loss of catalyst material.

Solid-State Hydrogen Storage: Advancements in Nanoporous Materials and Neutron Scattering Techniques

Authors: Haihua Wang$^{\text{None}}$; Mi Tian[1]; Oana Ghita$^{\text{None}}$; Valeska Ting[2]; Xiayi Hu$^{\text{None}}$

[1] University of Exeter
[2] The Australian National University

Emails for correspondence: m.tian@exeter.ac.uk, o.ghita@exeter.ac.uk, v.ting@bristol.ac.uk, whh@sust.edu.cn, xi- ayihu@xtu.edu.cn

Hydrogen, lauded for its potential as a clean energy carrier, occupies a pivotal position in the quest for sustainable energy solutions. Yet, the challenges tied to its safe and efficient storage persist, rendering conventional methods less suitable due to inherent safety risks and high operating pressures. An innovative avenue emerges in solid-state storage within nanoporous materials, which promises significantly enhanced storage densities and improved safety margins.

In this context, we present recent and ongoing research aimed at developing a robust solid-state hydrogen storage system using in situ neutron scattering [1, 2]. This cutting-edge approach has allowed us to provide physical evidence of solidified hydrogen confined in the optimal porous structure. Advanced in situ neutron scattering techniques have been instrumental in this discovery, illuminating the mechanisms at play within the porous materials.

Furthermore, based on the insights derived from this theoretical study, we have engineered porous composites with augmented hydrogen storage performance [3]. The marriage of theory and practical application in this research underscores the potential for solid-state hydrogen storage, opening new pathways toward realizing a more efficient and secure hydrogen energy landscape.

Microscopic understanding of stability and adsorption/separation of CO2 from flue gas by MOFs in real industrial conditions

M. Wahiduzzama[1] ,P. Lyu [1]; N. Heymans [2]; N. Garcia-Moncada [3]; G. Mouchaham [4]; M. Daturi [3]; G. De Weireld [2]; C. Serre [4]; Sabine Devautour-Vinot [5]; G. Maurin [1]

[1] ICGM, University of Montpellier, CNRS, France
[2] University of Mons, Belgium
[3] ENSICAEN, University of Caen, France
[4] IMAP, ENS, ESPCI Paris, CNRS, PSL University, France [5] ICGM CNRS/ENSCM/UM

In light of the current environmental situation, reduction of anthropogenic CO2 emissions from carbon-intensive industries like power plants, cement, steel, or petrochemical industries become one of the most pressing issues to combat global warming. Shifting towards a low-carbon economy requires cost-effective carbon capture utilization or sequestration (CCUS) technology to be developed. Currently utilized amine-based absorption-regeneration process suffers from high energy penalties for solvent regeneration. In this regard, adsorption-based processes are considered promising alternatives for CCUS. Metal-organic frameworks (MOFs) are a widely studied class of porous adsorbents that offer tremendous potential, owing to their large CO2 adsorption capacity and/or high CO2 affinity. However, the performances of MOF-based CCUS technologies have not been fully evaluated in real industrial conditions. For example, the industrial flue gas contains CO2, N2, H2O, and traces of other contaminants, such as H2S, SO2, and NOx, which compete for different adsorption sites or might impact the stability of the adsorbent materials. Therefore, it is crucial to understand the competitive adsorption of the various components of the flue gas. From an experimental standpoint, such study is tedious and time consuming while molecular simulations provide a quicker route to understand their adsorption behavior and plausible degradation at the microscopic level. In this presentation, I will outline a systematic joint computational/experimental approach to evaluate the stability and CO2 capture performance of a series of MOFs in the presence of various impurities within the framework of MOF4AIR, a multidisciplinary H2020 EU project. A more detailed analy- sis will be provided for a few top-tier MOFs that were selected for large-scale deployment in the industrial post-combustion capture process.

Acknowledgement:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 831975 (MOF4AIR project).

Understanding wetting and drying of nanoporous media through optical and dilatometry experiments

Juan Sanchez[1] , Laura Gallardo [1]; Yannick Tetzner [1]; Patrick Huber [2]

[1] Hamburg University of Technology (TUHH)
[2] Hamburg University of Technology and Deutsches Elektronen-Synchrotron DESY

Emails for correspondence: patrick.huber@tuhh.de, juan.sanchez@tuhh.de,
laura.gallardo@tuhh.de, yannick.tetzner@tuhh.de

While imbibition kinetics are well-understood in nanoporous materials [1], their drying dynamics are still under investigation [2]. In this study, we present time-dependent macroscopic dilatometry experiments on the deformation of nanoporous monoliths upon spontaneous, capillarity-driven infiltration of water as well as drying. During both processes, we find characteristic dynamical regimes that can be quantitatively described in terms of Laplace pressure effects and changes in the surface stress at the inner pore walls [3]. In the particular case of transparent nanoporous Vycor glass, additional imaging experiments are conducted, allowing direct optical access to the filling front. The observed wetting-drying dynamics are consistent with our analysis of the strain regimes. Our study demonstrates that it is possible to monitor the interplay of imbibition and drying dynamics by simple dilatometry measurements, provided proper humidity control.

References:

1. S. Gruener, T. Hofmann, D. Wallacher, A.V. Kityk, and P. Huber, Capillary rise of water in hydrophilic nanopores (Phys. Rev. E .), Stat. Nonlin. Soft Matter Phys., 79(6), (2009)
2. R. Al-Mandany, Experimental Study of Drying Process of Porous Materials (Conference paper: YUCOMAT2018) (2018)
3. G.Gor,P.Huber,andN.Berrnstein.Adsorption-induceddeformationofnanoporousmaterials—A review (Applied Physics Reviews) 4, 011303 (2017)

CH4/H2O Competitive adsorption in Nano porous materials under clathrate hydrate formation conditions

JYOTI SHANKER PANDEY[1] , Joaquin Silvestre Albero [2]

[1] DTU CHEMICAL ENGINEERING

[2] University of Alicante
Emails for correspondence: jyshp@kt.dtu.dk, joaquin.silvestre@ua.es

In this study, we delve into the intricacies of gas adsorption behavior within nanoporous materials, specifically focusing on the competitive adsorption of CH4 and H2O molecules under clathrate hydrate formation conditions. We aim to elucidate how the presence of water or humidity affects the total gas adsorption capacity of these materials.

Under low-temperature hydrate formation conditions, water tends to transform into gas hydrate crystals, thereby enhancing the overall gas storage capacity. However, this transformation process is far from straightforward and is heavily influenced by the properties of the nanoporous material, including its hydrophobicity, pore size, and surface chemistry. These material characteristics play pivotal roles in dictating the kinetics, overall storage capacity, and thermodynamics of the hydrate formation process.

To comprehensively examine CH4 gas storage and the competitive interactions with H2O molecules, we conduct a series of high-pressure reactor experiments. These experiments are designed to generate gas isotherms at low temperatures (1-2°C) across varying water saturation levels. Our primary focus is on understanding the profound impact of hydrophobicity and surface chemistry on the formation process within this hybrid system. Finally, we compare our results with those obtained from a bulk water system to affirm the synergistic effects of nanoporous materials on gas storage behavior.

Acoustic Response of Fluid Adsorption in Nanoporous Materials

Loriane Didier[1], Alan Sam [2]; Rodolfo Venegas [2]; Benoit Coasne [1] [1] CNRS/Univ. Grenoble Alpes

[2] Universidad Austral de Chile (UACh), Valdivia, Chile
Emails for correspondence: alan.sam@univ-grenoble-alpes.fr, loriane.didier@univ-grenoble-alpes.fr, rodolfo.venegas@uach.cl,

Email for correspondence: benoit.coasne@univ-grenoble-alpes.fr

Fluid adsorption and transport in nanoporous materials are at the heart of efficient technologies impacting our economy/ecology: energy storage/conversion, environment protection, health/human welfare, agribusiness/food science, etc. In particular, nanoporous solids shaped as membranes are expected to play a leading role in the "seven key chemical separations to change the world"1 but also to address increasingly complex problems such as bio/agropollutants removal, greenhouse gas mitigation, drinkable water production, etc. With the goal to design efficient processes based on an appropriate nanoporous material for a given application, the characterization of its textural and physicochemical properties is essential to establish reliable structure/property relationships. In this context, despite its generalized use in materials science, acoustics is often assumed to be unsuited for nanoporous due to their large wavelength compared to the pore size in this class of materials. Yet, the adsorption/permeation footprint of a nanoconfined fluid is included in an average way in the signal emitted by the system subjected to fluid pressure or acoustic excitation2 (see also recent review paper by Gor and coworkers on the elastic properties of confined fluids as probed using molecular modeling and ultrasonic experiments) [3].

In this work, we employ molecular modeling and theoretical approaches to unravel the acoustic signature of adsorption in nanoporous materials. Different fluid models (coarse-grained versus molecular descriptions) and with different interactions (CH4 versus CO2) are studied in a prototypical nanoporous material (zeolite) to probe pore size/interaction effects. We investigate the molecular mechanisms through which sound propagation and attenuation in nanoporous materials occur when subjected to fluid adsorption. Both dynamic structure factors and vibrational density of states for the fluid and solid phases are assessed to unravel the complex fluid/solid coupling at their interface and its impact on phonon modes (including their scattering which lead to sound attenuation). We will also discuss the implication of the acoustic signature of fluid adsorption for the characterization of nanoporous materials.

References:
[1] D. Sholl, R. Lively, Nature 532, 435-437 (2016).
[2] M. Miansari, J. Friend, Advanced Functional Materials 26(43) (2016).
[3] C. D. Dobrzanski, B. Gurevich, G. Y. Gor, Appl. Phys. Rev. 8, 021317 (2021)

Supercritical fluid activation and in-situ adsorption-microcalorimetric system to directly measure the gas adsorption amount, heat and kinetic data

Wentao Jiang[1]; liuliu long[1] , Yue-Biao Zhang [1]

[1] ShanghaiTech University

Emails for correspondence: jiangwt@shanghaitech.edu.cn, zhangyb@shanghaitech.edu.cn, liuliulong@163.com

Porous materials play a vital role in industrial and environmental systems due to their diverse applications. The adsorption capacity and associated heat during this process are crucial parameters for evaluating the performance of these materials. Achieving high sensitivity and accuracy is of utmost importance in adsorption and microcalorimetry instruments. As a result, researchers continuously strive to enhance the precision and repeatability of measurement results by employing various theoretical approaches to calculate the heat of adsorption.

In this work, we have designed a system for activating porous materials directly using supercritical extraction. The system involves mixing supercritical carbon dioxide with organic solvents and directly introducing them into the sample chamber to achieve rapid and efficient activation of porous materials with ultra-high surface area1. Additionally, we present a novel system comprising a Tian-Calvet microcalorimetry apparatus equipped with an automatic gas adsorption measuring unit or chemisorption instruments for in-situ measurement of physisorption and chemisorption heat, respectively2. To validate its feasibility and accuracy, we conducted experiments using different gases such as CH4, CO2 and C3H8. The obtained results effectively demonstrate the instrument's accuracy and convenience for mea- surements. Furthermore, this instrument allows us to accurately measure the evolved energy even at extremely low adsorption capacities, commonly referred to as "the zero-point adsorption heat." This valuable information sheds light on the most active sites within porous materials, thereby con- tributing to a better understanding of their properties.

References:

1. China, Design Patent, CN202011217334.6[P], Yue-Biao Zhang, Yu Tao, Zhaolin Shi, and Wentao Jiang, Porous material supercritical extraction device and method, 2022-05-06.
2. China, Design Patent, CN 111272806 A, Liuliu Long, Fan Yang, Jun Cai, Yihua Ran, Lunjia Zhang, A simultaneous adsorption and microcalorimetric device and method, 2020-06-12

Evaluation of a Commercial Chabazite-Type Zeolite Aging in the Industrial Process of Dehydration of Natural Gas CO2-Enriched

Kalil Kashefi[1] , Marcos Anacleto da Silva [2]; Vera M.M. Salim [2]; Frederico W. Tavares [3]; NEUMAN SOLANGE DE RESENDE [2]; Amaro G. Barreto [4]

[1] Universidade Federal do Rio de Janeiro
[2] Universidade Federal do Rio de Janeiro, PEQ
[3] Universidade Federal do Rio de Janeiro, PEQ, EQ [4] Universidade Federal do Rio de Janeiro, EQ

Emails for correspondence: vera@peq.coppe.ufrj.br, ftavares@peq.coppe.ufrj.br, kalil@eq.ufrj.br, neuman@peq.coppe.ufrj.br, anacleto@peq.coppe.ufrj.br, amaro@eq.ufrj.br

In this work, a commercial zeolite, in two states of fresh and aged, is considered for investigation. The aged sample obtained from an industrial natural gas (NG) dehydration plant was used as a reference. The effect of the aging process on the sample structure and the capability to perform the adsorption/desorption process were assessed using different characterization methods. Analytical and spectrometry techniques such as XRF, XPS, DRIFTS, and EDS/SEM were applied for elemental and bonding analysis, in addition to recognizing the type of carbon deposition. XRD was used to verify any structural changes during the aging process, and N2 adsorption/desorption was employed to measure the specific surface and volume of the samples [1,2].

Abundant adsorption/desorption cycles for the gas dehydration process showed that the aging mainly affected the activation of zeolite by hydrocarbon deposition. Minor changes, such as the size and migration of cations, were detected in the structures. The TGA curves for the chabazite zeolite used in the industrial plant showed the oxidation/burning of amorphous carbonaceous material (coke), between 250 and 400°C and the oxidation of carbonaceous material structurally organized in the temperature range of 400-700°C. Therefore, TGA identified the presence of coke deposition on the surface of the aged sample after use in the NG dehydration. The Temperature-programmed CO2 desorption (TPD-MS) showed significant deactivation of the adsorbent evidenced by the reduction in CO2 adsorption from 128.8 μmols/g to 13.6 μmols/g after the adsorption and regeneration cycles during the industrial operation of NG dehydration. The TPD-MS analysis was presented as an efficient technique to investigate the interaction of the adsorbent CO2 molecules with the solid surface of the studied zeolite, being an important tool for the evaluation of active surface sites. For this reason, TPD-MS can provide crucial information for the qualification of molecular sieves for the NG dehydration process.

Reference Isotherms using Reference Materials

H. Giang T. Nguyen,[1] Blaza Tolman,[1] Matthias Thommas[2] & Roger D. van Zee[1]

[1] National Institute of Standards & Technology, Gaithersburg MD 20899 USA
[2] Friedrich-Alexander-University Erlangen-Nürnberg, 91058 Erlangen, Germany
email for correspondence: roger.vanzee@nist.gov

Adsorbent materials have many applications, including those related to gas storage, gas purification, catalytic reforming, and sustainable development. Despite major progress in adsorption technology and physical adsorption characterization during the past two decades, measurement challenges still exist. For example, protocols for measuring high-pressure gas adsorption isotherms on well-characterized porous materials have not been standardized. To address these measurement needs, the Facility for Adsorbent Characterization and Testing ("FACT Lab") at the National Institute of Standards and Technology has undertaken a series of interlaboratory studies to measure and quantify adsorption isotherms using reference materials. Reference isotherms of carbon dioxide adsorption on ZSM-5 zeolite (NIST Reference Material™ 8852) have been determined, including as a function of temperature, to 4.5 MPa [1], [2]. Additionally, a reference isotherm for methane adsorption on zeolite y (NIST Reference Material™ 8850) has been determined, to 7.5 MPa [3]. Simple, empirical functions describing these isotherms were derived, and various physical properties of these zeolites have been studied [4]. More recently, isotherms for water adsorption on a nanoporous carbon (BAM Certified Reference Material P109) have been determined to 95% relative humidity and for neat water [5].

References:

1. H. G. T. Nguyen et al, Adsorption, 24 (2018) 531-539.
2. H. G. T. Nguyen, B. Toman, J. Colon Martinez, D. W. Siderius & R. D. van Zee, Adsorption 28 (2022) 15-25.
3. H. G. T. Nguyen et al, Adsorption, 26 (2020) 1253-1266.
4. H. G. T. Nguyen, R. Tao, & R. D. van Zee J. Res. Natl. Inst. Stan., 126 (2021) 126047.
5. H. G. T. Nguyen et al, Adsorption, 29 (2023) 113-126.

Acknowledgements:

The FACT Lab was established through funding from the Advanced Research Project Agency•Energy though an interagency agreement.

Converting Waste Tire to Activated Carbon Adsorbent Materials for Landfill Gas Purification

Brandyn Nutter[1] , Amirjavad Ahmadian Hosseini [1]; Laura Rojas [1]; Masoud Jahandar Lashaki [1]

[1] Florida Atlantic University

Emails for correspondence: bnutter2018@fau.edu, mjahandarlashaki@fau.edu,
aahmadianhos2021@fau.edu, lro- jas2021@fau.edu

Since 2013, the amount of scrap tire waste generated in the U.S. has increased by over 32%, while the utilization of materials derived from tire waste has decreased by over 25%. This has led to an increase in land disposal of tire waste by 123%. This trend necessitates the development of new methods and markets for processing and recycling scrap tires. One possibility, based on the sustainability princi- ples of industrial ecology, is to use tire waste as a source of carbon, which can be activated and used to make adsorbent materials which can be used in turn to purify landfill gas (LFG). LFG is generated when organic waste decomposes in the low-oxygen environment of a landfill. It is an unavoidable byproduct of the landfilling of municipal solid waste (MSW), and it is rich in methane (50-60 vol.%) and carbon dioxide (40-50 vol.%), with lower levels of hydrogen sulfide, water vapor, and siloxanes. Once purified, LFG can be used as renewable natural gas (RNG) to generate electricity or fuel the natural gas grid. The treatment of LFG into RNG is not only beneficial as a source of renewable energy but also benefits the environment by reducing greenhouse gas and odor emissions.

To explore the potential of using amine-modified adsorbent materials from waste tire-derived activated carbon (AC) to treat LFG, the following steps were taken. First, the waste tire was characterized to determine its composition and to identify any potential treatment or processing required before activation. Second, microwave heating was used to carbonize the tire in an oxygen-deficient environment, followed by converting the carbonized tire into AC. Third, N2 physisorption was used to explore the textural and structural properties of the AC, and multiple samples were selected for amine modification. Fourth, amine-modified activated carbon (i.e., aminocarbons) were synthesized with various amine types and loadings. Fifth, the potential of the synthesized aminocarbons for carbon dioxide adsorption was determined in the presence of dry carbon dioxide (30 vol.% in nitrogen), with multiple performant samples being chosen for further analysis. Sixth, the potential of the performant samples from the last step was further explored in the presence of humid carbon dioxide, with multiple performant samples being shortlisted for further evaluation. Seventh, the hydrogen sulfide adsorption potential of the previous performant samples was analyzed. Our preliminary results indicated that tire-derived AC materials are potential candidates to remove multiple impurities from LFG.

Improving the robustness and reproducibility of gas adsorption isotherm measurements on nanoporous materials

Author: Darren Broom[1]

[1] Hiden Isochema Ltd
Email for correspondence: dbroom@hidenisochema.com

Gas adsorption is commonly used to characterize the surface area, pore volume and pore size distribution of porous materials, as well as to assess adsorbents for use in gas storage and separation applications. Adsorption isotherms –plots of uptake versus pressure –can be measured using the volumetric and gravimetric techniques, and commercial instruments are widely available for this purpose. To determine the porous properties of materials, experimental isotherm data must then be analyzed using one of a number of different models. Despite the widespread availability of commercial instrumentation and the associated data analysis software, published results have been subject to irreproducibility [1-3]. This may be due to differences in the synthesis of different samples of the same material, material instability, measurement error, or inconsistencies in the analysis of experimental data [4]. This poster addresses the last two of these sources of irreproducibility, by describing five key steps that can be followed to make experimental gas adsorption isotherms on nanoporous materials more robust and reproducible [5].

References:

1. M.F.DeLange,T.J.H.Vlugt,J.Gascon,F.Kapteijn,Adsorptivecharacterizationofporoussolids: Error analysis guides the way, Microporous and Mesoporous Materials, 200 (2014) 199-215
2. D. P. Broom, M. Hirscher, Irreproducibility in hydrogen storage material research, Energy & En- vironmental Science, 9 (2016) 3368-3380
3. J. Park, J. D. Howe, D. S. Sholl, How reproducible are isotherm measurements in metal-organic frameworks? Chemistry of Materials, 29 (2017) 10487-10495
4. M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure and Applied Chemistry, 87 (2015) 1051-1069
5. D. P. Broom, How to make your research on gas adsorption in porous frameworks more robust and reproducible, 2024, manuscript under review

CPM9 | POSTER PRESENTATION
CATEGORY: MATERIALS

Densification and Validation of Binderless MOF Monoliths Based On Temperature-Pressure Swing Hydrogen Storage and Delivery Conditions

Author: Ruthradharshini Murugavel[1] Co-authors: Ali Rownaghi [2]; Fateme Rezaei [1]

[1] Department of Chemical & Biochemical Engineering, Missouri University of Science and Technology

[2] Department of Chemistry, Cleveland State University

Emails for correspondence: rezaeif@mst.edu, rmdhp@umsystem.edu, rownaghia@mst.edu

Transitioning to a sustainable energy source is the first and most crucial step in combating climate change. The critical bottleneck to using hydrogen (H2), an energy carrier, as a stationery and transportation fuel has been the development of materials capable of providing a viable storage capacity. Metal-organic frameworks are a class of crystalline materials composed of metal ions or clusters coordinated by organic ligands, structuring a highly porous material having a high surface area and porosity. Despite, having significant characteristics for practical implementation as viable materials for H2 storage, the poor packing of powdered MOF needs to be improved based on volumetric energy capacity. Thus, the densification of MOFs is crucial in reducing the void volume as they give way to enhanced gravimetric and volumetric storage capacities, improved kinetics, stability, and compatibility with storage tank designs. In this paper, we report the engineering of the best-performing high bulk-density monolithic MOFs in terms of their usable capacities, namely UiO-67 and MOF-177, without binders or pressure compaction. After shaping, monolithic MOF-177 and UiO-67 stores up to 49.95 g/L and 47 g/L at 77 K and 100 bar and deliver up to 47.02 g/L and 44 g/L operating in a combined temperature-pressure swing (TPS) delivery conditions between 77 K/100 bar 160 K/5 bar. These findings substantially improve the deliverable capacities of the mechanically robust densified MOFs based on onboard storage applications.

Self-template Synthesis of Nanoporous Carbons from π-conjugated Ionic Liquids with Molecular Nanocarbon Functionalities

Ryusuke Futamura[1],Toshinori Seki [1]; Kento Nakamura [1]; Ryuta Sekiguchi [2]; Taku Iiyama [1] [1] Shinshu University

[2] Hirosaki University
Email for correspondence: ryu_f@shinshu-u.ac.jp

Nanoporous carbons gather much attentions as a key material for the achievement of Sustainable Development Goals (SDGs), because of the high volumetric capacities and the molecular sieving characters for industrially important gas molecules, like CH4 and CO2. Recently, the synthesis of various types of nanoporous carbons has been reported, including top-down synthesis by activation of variety of parent carbon matrix and bottom-up synthesis by chemical vapor depositions of hydrocarbons. In particular, one can obtain distinctive nanoporous carbon materials with controlled pore sizes and uniformed pore geometries from hard template synthesis methods with periodic mesoporous silica and zeolite. However, there are some problems on the template synthesis because of the harmful mold removing process using highly corrosive agents like HF. Here, we report the possibility of seif-template synthesis of nanoporous carbons from π-conjugated ionic liquids with molecular nanocarbon functionalities without the harmful mold removing process.

Ionic liquids (ILs) are room-temperature molten salts which exist in a liquid state without any solvent molecules. One of the most important characteristics of ILs is the diversity of the chem- ical compositions and the structures because of the organic-inorganic hybrid materials. Recently, our group have synthesized a new type of ILs in which π-conjugated molecular nanocarbons like naphthalene are introduced in the cation flameworks, and we call them π-conjugated ILs. Since the π-conjugated ILs are expected to have the both characteristics of molecular nanocarbons and of ILs, we have clarified the relationship between the photo-luminescence properties and the domain structure formation of the naphthalene moieties of π-conjugated ILs.

Furthermore, we could succeed to synthesize a porous carbon with both meso- and micro-porosities only by heat treatments of the π-conjugated IL without any template materials. The porosity could be originated from the domain structure of molecular nanocarbon moieties existing in π-conjugated ILs themselves. This fact indicates that we can precisely control the structures of porous carbon flameworks by using variety of π-conjugated ILs as a precursor. In our presentation, we will dis- cuss the characteristics of the porous carbon and the relationship between the porosity and the microscopic structure of the precursor material of π-conjugated IL from hybrid reverse Monte Carlo simulation-aided X-ray scattering technique.

Investigating the effect of the extra-framework cation on propane / propylene adsorption in LTA zeolites

Claessens Benjamin[1],Emily Bloch [1]; Gabriel Trierweiler-Conçalves [2]; Gerald Chaplais [2]; Jean Daou [3]; Jean-Louis Paillaud [2]; Mohammed-El Amine Benchaabane [4]; Sandrine Bourrelly [1]

[1] Aix-Marseille University, CNRS
[2] Université de Haute-Alsace, CNRS [3] Aptar Technologies
[4] Aix-Marseille University

Email for correspondence: benjamin.claessens@univ-amu.fr

The separation of propane and propylene remains a challenging seperation process, due to the similar boiling points and size of both molecules. LTA zeolites have been shown to be promising adsorbents, but a systematic study of the effect of the extra-framework cations on propylene and propane adsorption is lacking.

In this work, we prepared LTA zeolites exchanged with different cations (Na+, Li+, Ca2+, Mg2+, Cu2+, Mn2+, Zn2+). All exchanged samples were synthesized with Na+ as counterion and then par- tially exchanged with the other cation (30% and 50%). Results were compared with a pure Si-LTA zeolite. Adsorption isotherms were measured using a manometric system, coupled to an isothermal microcalorimeter (Tian-Calvet type), allowing the simultaneous measurement of the released heats of adsorption. While Si-LTA shows no preferential adsorption of propane or propylene and is essentially heterogeneous for both probe molecules, propylene shows a strong interaction with divalent cations. On the other hand, LTA zeolites with monovalent cations (Na+ / Li+) show slow diffusion of propane, opening perspectives for a kinetic separation.

Carbon Dioxide Capture in NaOH-Impregnated Activated Carbon

Prapatsorn Borisut[1], Atichat Wongkoblap [1] ; Chaiyot Tangsathitkulchai [1] ; Aroonsri Nuchitprasitchai [1] ; Krittamet Phothong

[1] Suranaree University of Technology

Email for correspondence: atichat@sut.ac.th

Carbon dioxide (CO2) adsorption at high pressures by alkali-impregnated activated carbons were studied in this presentation. Four types of activated carbon were prepared with two-step activation method and activation combined with oxidation method [1] and then impregnated in different concentration of alkali solution of 1, 4, 7 and 10%. The results of CO2 adsorption at 0°C up to saturated pressure show that the maximum adsorption capacity was obtained from the activated carbon prepared by activation combined with oxidation method with 180 minutes of total activation time, two cycles for oxidation and 1% NaOH impregnation. The BET surface area of all activated carbons decreased with an increase in NaOH loading. Micropore volume of all activated carbons is maximum when impregnated with 1% NaOH. It is seemed that the impregnation with appropriate NaOH loading can develop some micropore on activated carbon surface and lead to an increase in micropore volume.

Metal Organic Framework Hollow Fibers for CO2 adsorption and Chemical Warfare Agent Degradation

Author: John Landers[1]

[1] Apollodyne
Email for correspondence: admin@apollodyne.com

MOFs are excellent candidates for the capture of CO2, in particular for the environmental control for life support systems in space suits and onboard the space shuttle. Traditionally, beads of lithium hydroxide, zeolites or polyamines have been employed for CO2 removal for the aforementioned applications. However, the use of beads can generate unfavorable large pressure drops. By employing a high CO2 capacitance material such as MOF-74 in a novel form factor such as a hollow fiber we have fabricated a composite with a higher than conventional CO2 capacitance that also alleviates large pressure drops. Using a customizable injection molding process developed in-house, we can control the dimensions of the hollow fiber (inner diameter, fiber wall, MOF loading) by tuning a combination of parameters both at the macroscopic and nano scales. With the ability to fine tune fiber dimensions and properties, the transport phenomena (CO2 vapor) through the fibers, and sub- sequently through fiber arrays can be precisely controlled. Our approach is sub divided into three aims and are as follows: 1) fiber dimensions can be controlled through a combination of nanoscale and macro scale parameter tuning, 2) tuning of the fiber dimension results in difference performance for mass transfer, and 3) multiple fibers can be bundled into an array resulting in an flow through the array that approximates laminar flow. The fibers resulting from these aims have been charac- terized by N2, CO2 adsorption, X-ray diffraction and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) in order to assess the structure-performance relationships of the fibers. The development of these metal organic framework hollow fibers have broad implications beyond filtra- tion, and may serve as a lightweight alternative to conventional filtration media employed the across the defense, space and healthcare industries.

Hydrophobic metal-organic frameworks with new fluorinated ligands

Vladimír Zeleňák[1] , Dávid Princík [2]; Adriána Zeleňáková [2]
[1] Faculty of Natural Science, Pavol Jozef Safarin University in Kosice, Slovakia

[2] Faculty of Science, P. J. Šafárik University, Moyzesova 11, Košice, Slovak Republic
Emails for correspondence: vladimir.zelenak@upjs.sk, david.princik@upjs.sk,
adriana.zelenakova@upjs.sk

The robustness and reactivity of a metal-organic frameworks depend on metal-ligand interactions, where the metal-containing clusters may be vulnerable to ligand substitution by water, leading to the framework collapse upon exposure to moist air. This instability limits the practical uses of many MOFs. In order to further enhance the stability of the framework, many different approaches. One of the approaches to synthesize moisture-stable MOFs is use of hydrophobic linkers. The fluorinated MOFs are such option [1]. A novel fluorinated lanthanide-based metal-organic frameworks (Ln-F-MOFs) were constructed from the deprotonated 3,3'-difluorobiphenyl-4,4'-dicarboxylic acid (H2L1) or the deprotonated 3,3'-bis(trifluoromethyl)- [1,1'-biphenyl]-4,4'-dicarboxylic acid (H2L2), see Fig. 1a [2]. Using the acids H2L1 or H2L2 and lanthanide ions, the complexes with the composition {[M2(L1 or L2)3(DMF)2]·xDMF·yH2O}n (M= Dy,Tb, Ho, Er, Eu for L1 and Ce, Pr, Nd, Gd, Eu for L2) were prepared.

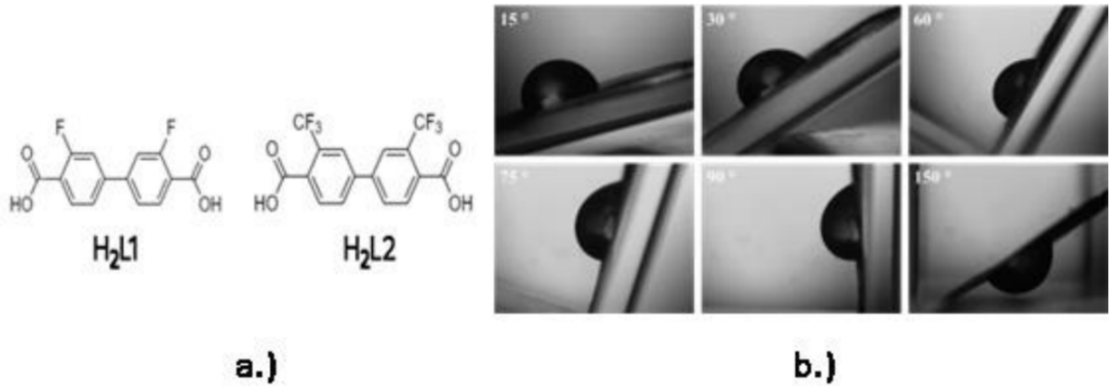


Fig. 1 a.) Structural formulas of acids H2L1 and H2L2. b.) Contact angle droplet test.

These complexes show high surface hydrophobicity with "rose petal effect"(see Fig. 1b), thermal stability up to 300 °C and photoluminescence properties determined the characteristic f-f transitions for the individual metal ions. The porosity of some activated coordination polymers was studied by N2, CO2 and H2 adsorption isotherms. In compounds containing Pr(III), Gd(III) and Eu(III), the magnetic properties were investigated. The detailed information will be presented at the conference.

References:

1. M. Bosch, M. Zhang, H.-C. Zhou. Increasing the Stability of Metal-Organic Frameworks, Advances in Chemistry, (2014) 18232746.
2. D. Princík, V. Zeleňák, J. Bednarčík, J. Elečko, J. Macko, T. Zelenka, R. Gyepes, E. Dutková, Novel fluorinated MOFs with hydrophobic properties, Polyhedron, (2023) 116739.

Acknowledgements:

This work was supported by the Scientific Grant Agency of the Slovak Republic (VEGA) under Project 1/0865/21 and by the Slovak Research and Development Agency under Contract APVV-20- 0512.

Development of novel porous geopolymer monoliths based on Moroccan oil shale for effective removal of heavy metals (Zn (II), Cu (II), Pb (II)) from wastewater.

said mansouri[1],SANAE SBI [1]; JONES ALAMI [1]; HASSAN HANNACHE [1]; YOUSSEF TAMRAOUI [1]

[1] Mohammed VI Polytechnic University, Benguerir

Email for correspondence: said.mansouri@um6p.ma

This study presents the synthesis of Porous Geopolymer Monoliths (PGMs) through the utilization of metakaolin (MK) and oil shale (OS) as raw materials. MK contributed aluminosilicates, while OS played a multifaceted role, acting as a pore-forming agent upon mixing with phosphoric acid, enhancing the selectivity of geopolymers towards organic pollutants and heavy metals, and aiding in the sustainable utilization of local natural resources. Employing experimental design method- ology, we systematically optimized the synthesis conditions of these geopolymer monoliths, systematically investigating the influence of critical factors, including the solid-to-liquid ratio (L/S), oil shale mass percentage, and phosphoric acid molar concentration. The resulting adsorbents underwent rigorous evaluation, encompassing apparent porosity measurements and assessments of their methylene blue adsorption capacity. Additionally, we assessed the optimal material's performance in the removal of heavy metals from wastewater. An extensive array of characterization methodologies, such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis, optical microscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and UV-visible spectroscopy, was employed to comprehensively analyze the produced geopolymers. Our research findings unveiled that the highest heavy metal adsorption was achieved with monolithic geopolymers prepared under specific conditions, characterized by L/S=1.08, OS=7.5%, and [H3PO4]=9.76M. These conditions demonstrated remarkable adsorption metrics, with rates of 12.5 mg/g for Cu(II), 33.3 mg/g for Pb(II), and 30.30 mg/g for Zn(II), all aligning with the expectations set by the Langmuir model.

Sorption of SF6 and SO2 on Modified Zeolites Materials

Katarzyna Zarębska[1],Mikihiro Nomura [2]; Megumi Irie [2]; Jakub Szczurowski

[1] Faculty of Environmental Engineering, Geomatics and Renewable Energy, Kielce University of Technology, 25-314 Kielce, Poland

[2] Shibaura Institute of Technology, Department of Applied Chemistry
Emails for correspondence: lscathy@shibaura-it.ac.jp, mg22003@shibaura-it.ac.jp, szczurow@agh.edu.pl, zarebska@agh.edu.pl

Information about the porous nature of adsorbents is important for understanding the pore structure of solids. Adsorption is widely used as a probe for pore structure. The measured adsorption behavior of a sample reflects, in an aggregated manner, the adsorption behavior of individual pores. Sulfur hexafluoride (SF6) and SO2 are industrial gases used in various applications. Compared to CO2, they are among the most common gases whose presence is harmful in the atmosphere. Their conventional capture methods are costly due to the energy required for phase transitions. These two gases differ not only in their chemical nature but also in their structure, size, and shape, factors that significantly affect transport and adsorption capacity.

In this study, the sorption of SF6 and SO2 was investigated on several selected inorganic materials. Experimental studies of sorption isotherms at 298K showed that, for both sorbates, higher sorption values were obtained for SO2 over the entire pressure range. Tests were conducted on samples belonging to two material topologies: faujasite (FAU) and MFI-type frameworks, whose structures differ in pore size and connectivity. This paper presents experimental data and proposes a mathematical description of the sorption process. These materials behave like molecular sieves and can be used for quite selective adsorption of the relevant gases. Furthermore, modification of the faujasite with organic silane resulted in a drastic reduction of the sorbent's surface area, leading to significantly lower sorption capacities for gases. This research is important not only for practical applications but also for modeling and predicting sorption processes, considering not only the effects of molecular sieves but also the influence of surface nature and interactions with polar and non-polar molecules.

Acknowledgements:
Funding: The project was carried out within the OPUS 2022. This research was fully funded by the National Science Centre, Poland, grant number OPUS-22 UMO-2021/43/B/ST8/01636.

Trapped in the CO2 Loop: A Study of Carbon/MOF Composites for Direct Air Capture (DAC)

Jakub Szczurowski[1] , Adrian Lubecki [1]; Katarzyna Zarębska [2]; Patryk Bartulik [1]

[1] Faculty of Energy and Fuels, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow, Poland; szczurow@agh.edu.pl

[2] Faculty of Environmental Engineering, Geomatics and Renewable Energy, Kielce University of Technology, 25-314 Kielce, Poland; kzarebska@tu.kielce.pl

Emails for correspondence: pbartulik@student.agh.edu.pl, lubecki@agh.edu.pl, szczurow@agh.edu.pl, zarebska@agh.edu.pl

In response to the high demand for effective carbon dioxide (CO2) mitigation and removal strategies, this study addresses the development and characterization of new materials - carbon/MOF (Metal-Organic Framework) composites. These materials represent a significant advance in the field of direct air capture (DAC) technology, offering a promising avenue to address growing concerns about elevated CO2 levels in the atmosphere. This study presents a comprehensive synthesis and characterization of carbon/MOF composites, tailored for efficient CO2 capture in DAC applications. We started our research by developing a new method for synthesizing carbon/MOF composites. This method focused on optimizing porosity and surface area, key factors for efficient CO2 adsorption. The synthesized composites were then characterized to clarify their textural properties. Porosity was mainly analyzed using argon adsorption isotherm measurements, which provided detailed insight into the pore size distribution and surface area of the composites. The main focus of our research was to evaluate the CO2 adsorption isotherms of these materials at different temperatures: 273K, 298K and 323K. These temperatures were chosen to simulate the range of environmental conditions in which DAC systems can operate. CO2 adsorption isotherms at these temperatures offer a clear picture of the CO2 capture efficiency. In addition to these measurements, we also focused on the isosteric heat of adsorption, a key parameter in assessing the energy efficiency of the adsorption process. This parameter provides insight into the strength of the interaction between CO2 molecules and the adsorbent. Higher isosteric heat indicates stronger interactions, which may be beneficial for initial CO2 capture, but may require more energy to regenerate. Our results showed significant differences in adsorption capacity and isosteric heat, highlighting the temperature-dependent behavior of these materials in CO2 capture and the energy implications of their use in DAC systems. The study not only reinforces the potential of these materials in environmental applications, but also sets the foundation for future research to improve the performance and scalability of DAC technol- ogy a crucial step in breaking free from the CO2 loop. Addressing scalability and cost challenges is essential for advancing DAC technology. Research into adsorbent regeneration and durability will enhance real-world application, paving the way for successful, efficient CO2 mitigation. Our findings demonstrate significant advances in DAC technology, offering a hopeful outlook towards successfully addressing the global challenge of elevated atmospheric CO2 levels.

Acknowledgements:
Funding: The project was carried out within the OPUS 2022. This research was fully funded by the National Science Centre, Poland, grant number OPUS-22 UMO-2021/43/B/ST8/01636.

Applications of MOFs for the chemical warfare agents (CWAs) simulant adsorption

Emily Bloch[1] , Guillaume Maurin [2]; Lotfi Boudjema [1]; Sandrine Bourrelly [1]

[1] Aix-Marseille University - CNRS MADIREL

[2] Institut Charles Gerhardt Montpellier, UMR-5253, Université de Montpellier
Emails for correspondence: emily.bloch@univ-amu.fr, sandrine.bourrelly@univ-amu.fr,
guillaume.maurin1@umontpellier.fr

Chemical warfare agents (CWAs), such as sarin and sulfur mustard, VX chemical components lead to death with only traces of a few micrograms. The use of rapid decontamination of these compounds under harsh conditions remains a great technological challenge. Adsorption is still considered one of the most efficient methods that can be chosen to adsorb such compounds. Metal–Organic Frameworks (MOFs) are efficient materials for the decontamination of CWAs because of their high porosity and tunable reactivity [1]. In this study, a serie of stable MOFs, differing in surface area/pore volume, secondary building unit (SBU) connectivity, defects, pore functionalization, and open metal sites were examined in order to assess their adsorption performances. The simulants of CWAs have been taken to mimic the real CWAs [2]. The adsorption microcalorimetry and the force field Monte Carlo simulation are employed to understand the adsorption behaviours of these systems.

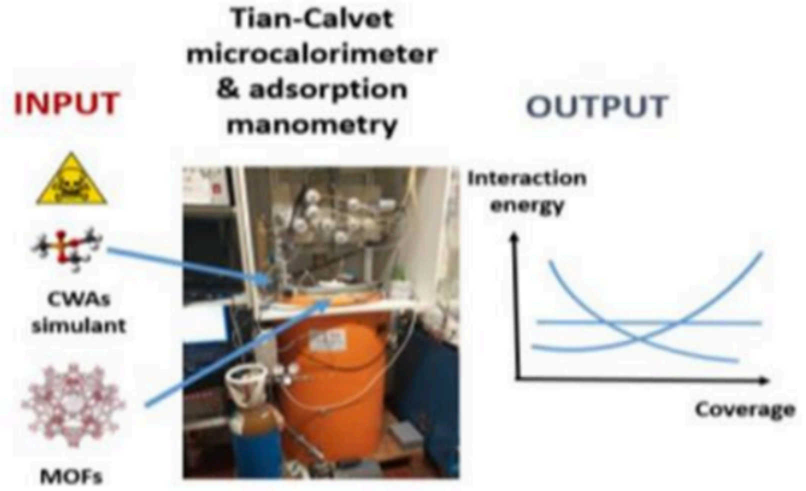


Fig. 1. Adsorption microcalorimetry combines adsorption manometry with a Tian-Calvet microcalorime- ter, allowing the direct measurement of adsorpion energies as a function of amount adsorbed

References:
[1] Hong-Cai Zhou, Jeffrey R. Long, and Omar M. Chem. Rev. 112, 2, 673–674, 2012.
[2] C. Vieira Soares, A.A. Leitão, G. Maurin. Microporous and Mesoporous Materials, 280, 97-104, 2019.

3D-printed hybrid zeolite structures constructed by a phase inversion process

Ben Sutens[1] , Marleen Rombouts [1]; Steven Mullens [1]; Yoran De Vos [1]

[1] VITO
Emails for correspondence: marleen.rombouts@vito.be, steven.mullens@vito.be,
ben.sutens@vito.be, yoran.devos@vito.be

Additive manufacturing is gaining increasing interest in the field of catalysis and gas separation applications due to the geometric flexibility for a wide range of materials. However, this process typically demands the use of a combination of organic and inorganic binders such as clays, silica or alumina to ensure mechanical integrity. As a result, these types of structures often are extremely brittle and require several post-processing steps involving thermal decomposition of the organic content which could lead to poor adhesion between the various components. In this work, hybrid organic-inorganic composites were developed using the 3D micro-extrusion technique in combination with a phase inversion process. Due to the combination of the capture efficiency of the inorganic materials and the flexibility or toughness of a polymer matrix, a non-brittle hybrid composite adsorbent composed of a polymer skin encapsulating the uniformly distributed inorganic particles could be developed. Moreover, the ability to eliminate the required thermal treatment in conventional binder systems enables the direct shaping of a wide range of materials that are susceptible to oxidation or thermal decomposition including carbon-based materials, metals and various types of metal-organic frameworks (MOFs).

As a model case, zeolite 13X was used for H2O and CO2 adsorption while three different polymers were compared to evaluate the effect of the polymer nature on the porosity and zeolite accessi- bility. Extensive characterization was performed in terms of N2, Ar and Hg porosimetry as well as static isotherm measurements and dynamic breakthrough curves. The developed polymer com- posites were compared with a 3D-printed zeolite-clay structure and other conventional structured zeolites, including pellets and wash coated honeycombs, to show the promising potential of this approach and the industrial applicability.

Novel nanoporous composites for hydrogen storage

Alex Pennetier[None]; Jean-Philippe Torré[None]; Laurent Perrier[None]; Christelle Miqueu[1]

[1] Université de Pau et des Pays de l'Adour
Emails for correspondence: cmiqueu64@gmail.com, laurent.perrier@univ-pau.fr

Given the current environmental problems, renewable energy resources (such as photovoltaics or wind power) are now an absolute necessity. However, the intermittency of these resources in the production of electricity is a key factor and energy storage and efficient energy conversion systems are required. In this context, hydrogen could be used as a vector energy for renewable energy. Indeed, hydrogen can be produced by electrolysis and then the energy contained in this molecule can be released thanks to a fuel cell. But to achieve this, the issue of hydrogen storage needs to be overcome.

Organic molecular crystals, like hydroquinone clathrates, could be promising hydrogen storage materials. Clathrates are supramolecular compounds consisting of a guest molecule (here H2) and cavity-forming host molecules. The formation of hydroquinone (HQ) clathrates with gases such as CO2 [1] or CH4 [2] is well known in the literature. But, for hydrogen capture, some important restrictions limit the development of this material, like high pressures and low kinetics of clathrate formation. Han et al. [3] were able to obtain a hydrogen HQ-clathrate by pre-forming a guest-free structure, and then filling it with H2 at 350 bar. Other attempts were done to improve the storage capacity of hydroquinone clathrate, like the addition of C60 [4] but not optimal system has been found to date. The strategy developed in this work consists in the impregnation of hydroquinone inside the micropores of a porous material in order to use the confinement effect both to initiate the formation of the confined clathrates and to improve the kinetics of enclathration. To do so, a novel method of impregnation is developed and tested on several materials of different chemical nature (carbon, polymer, silica) and having various pore size (between 1 and 15 nm). TGA-DSC, Argon porosimetry and MAS-NMR are used for the characterization of the new composites. The impregnation rate of organic crystals can reach up to 35% by mass of the hybrid material. For the case of HQ impregnated in a porous polystyrene-based material, the formation of the HQ clathrate can be reached with cycling the temperature between 0 and 100°C. The storage capacity of the sample increases from 0.1 to 1.3 wt.% per gram of sample (or 7 wt.% per gram of HQ) of H2 in ten temperature cycles. Moreover, the system is stable at room temperature and P = 1 bar of H2 with a storage capacity of 5.7wt.% of H2 per gram of HQ and H2 can be totally released at 100°C. Similar storage capacities are also obtained with other materials such as MCM-41+HQ.

In situ pXRD monitoring of compliant MOFs under combined mechanical and gas pressure

Paul IACOMI[1]; Pascal Yot[2] ,Christian Serre [3]; Frederico Alabarse [4]; Sujing Wang [3]; Guillaume Maurin [5]

[1] Surface Measurement Systems

[2] ICGM, Univ. Montpellier, CNRS, ENSCM, 34095 Montpellier, France

[3] Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS PSL University, 75005 Paris, France

[4] lettra Sincrotrone Trieste Basovizza, 34149 Trieste, Italy [5] Université Montpellier/CNRS

Emails for correspondence: piacomi@surfacemeasurementsystems.com, dburnett@surfacemeasurementsystems.com, guillaume.maurin1@umontpellier.fr

Compliant MOFs are known to respond to external stimuli, such as pressure, temperature, and adsorbed guests by undergoing remarkable structural changes [1]. Here, the coupling of two or more stimuli presents the opportunity of tuning a process like gas separation, affording control over the un- derlying framework's state [2]. However, structural information of materials undergoing combined guest adsorption and mechanical pressure application has been insofar limited to closed-system di- amond anvil cells [3].

We here detail a unique clamped diamond window cell prototype specially developed for use with soft porous materials. For the first time, uniaxial mechanical pressure (up to 0.5 GPa) and gas dosing (up to 20 bar) were combined in an in-operando PXRD experiment, where the two stimuli can be decoupled and independently controlled. The cell was first validated using reference materials (NaCl and SiO2), followed by a study of a CO2 sorption under pressure in the metal-organic framework MIL-53, known to undergo "breathing"compliance under both stimuli [3,4]. The cell allowed a direct observation of MIL-53 phase existence throughout a gas-mechanical pressure space. In particular, it was possible to obtain tentative evidence that mechanical pressure can maintain this material's pores in a closed state throughout gas adsorption, confirming previous experimental and computational results [2].

References

[1] Z. Liu, et al., Chem. Commun., 56, 66, (2020) 9416–9432; [2] N. Chanut et al., Nat Commun, 11, 1, (2020) 1216; [3] V. Bon et al., Adv. Funct. Mater. 30, (2020) 1907847. [4] S. Bourrelly et al., JACS, 127, 39 (2005) 13519–13521; [5] P. G. Yot et al., Chem. Commun. 50, 67 (2014) 9462–9464.

Impact of Carbon Content in Single-Wall Carbon Nanotube-Titanium Dioxide Composites Interfacial Modulation and Catalytic Behavior

Coset Abreu Jauregui[1], Antonio Sepúlveda-Escribano [1]; Joaquín Silvestre-Albero [1]

[1] University of Alicante
Emails for correspondence: joaquin.silvestre@ua.es, asepul@ua.es, coset.abreu@ua.es

Advanced oxidation processes driven by natural sunlight are the key to the next generation of water treatment technologies. Photocatalysis using semiconductor materials constitutes a promising approach to degrade organic contaminants in wastewater with minimal generation of secondary pollutants. In this scenario, carbon-based nanomaterials have emerged as promising modifying co-catalysts. The incorporation of the carbon structure manages to enhance the photocatalytic activity under visible light and the overall yield of the reaction. The improved behavior is attributed to the adsorption behavior associated with this type of nanostructures and the newly developed highly-extended heterojunction. More specifically, single-walled carbon nanotubes (SWCNTs) have been anticipated as superior modifiers to enhanced the photocatalytic performance of catalysts like TiO2. However, the characterization of the synthesized photocatalysts unveiled intriguing interfacial phenomena directly associated with the presence of important electronic effects at the interface. With these premises, this study presents a comprehensive investigation into the effect of the quantitative modification of commercial titanium dioxide - P25 - using four distinct ratios of single-walled carbon nanotubes (SWCNTs) 5, 10, 20, and 30 % w/w. Physicochemical characterization revealed a porosity-constrained material with high crystallinity and well-disperse titania-carbon phases. In particu- lar, XPS analysis suggests augmented electron-hole mobility at the carbon/oxide interface, which was also confirmed by RAMAN spectroscopy. The photocatalytic performance was assessed for Rhodamine-B (RhB) removal. Overall, complete degradation was achieved promptly under visible-light exposure. These promising results are attributed to intrinsic physicochemical alterations at the formed heterojunction structures and the composite's dual-role capability of simultaneous adsorption and photodegradation of RhB. Notably, the induced structural features are in correspondence with the composite's potential for improved photocatalytic performance. These findings validate our initial hypothesis and underscore the crucial importance of thoughtful design in synthesizing photocatalytic materials, particularly for applications aimed at environmental remediation.

References:
1. J. Zhang, M. Vasei, Y. Sang, H. Liu, J.P. Claverie, TiO2@carbon photocatalysts: The effect of carbon thickness on catalysis, ACS Appl. Mater. Interf., 8 (2016) 1903-1912
2. P. Suyana, P. Ganguly, B.N. Nair, S.C. Pillai, U.S. Hareesh, Structural and compositional tuning in g-C3N4 based systems for photocatalytic antibiotic degradation, Chem. Eng. J. Adv., 8 (2021) 100148
3. S.S. Ghumro, B. Lal, T. Pirzada, Visible-light-driven carbon-doped TiO2-based nanocatalysts for enhanced activity toward microbes and removal of dye, ACS Omega, 7 (2022) 4333-4341

Acknowledgements:
Authors acknowledge financial support from MINECO (PID2019-108453GB-C21) and MCIN/AEI/10.13039/501100011033 and EU "NextGeneration/PRTR (Project PCI2020-111968/ERANET-M/3D-Photocat).

Tailoring the Adsorption Properties of Hierarchical Porous Silicas for High-Capacity Water Sorbents

Pasquale Fulvio[1] , JiaJi Lin [1]; Krista Walton [1]

[1] Georgia Institute of Technology
Emails for correspondence: pfulvio@gatech.edu, jlin650@gatech.edu, krista.walton@gatech.edu

Hierarchical mesoporous-macroporous silica materials (HS-PEG) were prepared via a one-pot hydrothermal synthesis method using tetraethyl orthosilicate (TEOS) as the silica source, NH4OH as condensation catalyst, and a combination of alkylammonium bromide surfactants (CnTAB) and different polyethylene glycols (PEG) as structure directing agents (SDAs). Once the SDAs were removed by calcination in air, periodic and wormhole mesopores within primary particle units, and macropores formed by particle agglomerates were obtained. Similar to MCM materials [1], we report the control over the mesopore size using different alkyl chain lengths within 2 to 4nm range. Moreover, the solvent system used, namely, water, and water-ethanol, also dictated the adsorption properties of the materials. For instance, when water was the single solvent used, mesopores were nearly 1nm larger and pore volumes were nearly double than the counterparts prepared in water-ethanol. Higher ratios of NH4OH also led to higher mesopore volumes. Hygroscopic salts including anhydrous LiCl, MgCl2, MgSO4, CaCl2, and SrCl3.6H2O and SrBr3.6H2O, were then impregnated in these silicas by a modified incipient wetness method with pre-determined salt to silica weight ratios. For LiCl containing composites, the water uptake increased proportionally to the LiCl target contents [2]. Moreover, composites having different pore volumes and pore widths were found to adsorb similar amounts of water. The composites were found stable for salt loadings of up to 60wt.%. As for Mg salts, composites did not deliquesce for loadings of less than 40wt.%. Such salts form hydrates as MgCl2.6H2O and MgSO4.7H2O, that have larger unit cells, and cannot be dehydrated unless thermally treated to temperatures greater than 300oC, which exceed the operation range of atmospheric water harvesting (AWH) or of thermal energy storage (TES) devices. These results indi- cate that the free mesopore volume in the composites is required for the strong nanoconfinement of salt hydrates, and to the high-water uptakes exceeding 150wt.% at 80% relative humidity, as in case of LiCl composites. Finally, the current synthesis method for HS-PEG represents an improvement over previously reported monolith syntheses [2, 3] that required multiple steps. The present method yields powders with fine distributions of sizes, and that can be easily integrated with AWH or TES devices.

References:

1. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc., 114 (1992) 10834-43.
2. C Chen, J. L. Salinger, M. E. Essig, I. M. Walton, P. F. Fulvio, K. S. Walton, Hierarchical silica composites for enhanced water adsorption at low humidity conditions, ACS App. Mater. Interfaces, under review.
3. J. H. Smått, S. Schunk and M. Linden, Versatile Double-Templating Synthesis Route to Silica Monoliths Exhibiting a Multimodal Hierarchical Porosity, Chem. Mater., 15 (2003) 2354-2361.

Acknowledgements:

The authors acknowledge financial support from the DARPA Advanced Research Project Agency Atmospheric Water Extraction Program under Grant No. HR001120S0014.

Quantifying Structural Rigidity in Metal–Organic Frameworks with Increased Linker

Dimensionality Courtney Smoljan[1]; Omar Farha[1]; Randall Snurr[1]

[1] Northwestern University
Emails for correspondence: courtney.smoljan@northwestern.edu, snurr@northwestern.edu

Given that chemical separations account for 15% of the world's total energy consumption, it is critical to design energy-efficient pathways for the purification of chemical mixtures.1 Membrane separations and adsorption processes are promising nonthermal alternatives to energy-intensive separation technologies, as they separate molecules by size or chemical affinity. Metal–organic frameworks or MOFs are some of the best materials for these applications due to their nanoporosity and high tun- ability. When tuning MOFs toward separating molecules with sub-Ångstrom differences in size, a common challenge in industrial separations, defining a MOF's local pore environment is the most important factor. However, researchers typically focus on the dimensionality of the overall structure when designing MOFs, rather than considering the dimensionality effects of the linker component itself. We sought to leverage increased linker dimensionality to achieve precise, nano-scale con- trol over a MOF's pore size by mitigating effects of structural flexibility. Specifically, 3-dimensional linkers (3DLs) are sterically bulky, preventing global breathing transitions in MOFs. Additionally, they occupy the same amount of space, regardless of their orientation, alleviating the impact of linker rotation on pore size.2 Our groups have demonstrated that installation of 3DLs in structures analogous to MIL-53 –a structure known for its flexibility –results in global rigidity, allowing them to separate molecules with sub-Ångstrom differences in size, like hexane isomers and xylene iso- mers.3,4,5 Herein, we aimed to investigate the relationship between linker bulkiness and rigidity by using variable pressure X-ray diffraction studies to quantify each material's bulk modulus. Addition- ally, we used density functional theory (DFT) calculations to generate electronic energy profiles for MIL-53 and its 3DL isostructural analogues. These electronic energy profiles show energies obtained from fixed volume geometry optimizations as a function of unit cell volume. Finally, we used DFT to derive the elastic constants of these materials, which were used to calculate values of Young's moduli and to better understand the structural dynamics of these frameworks.

Carbon Dioxide Capture from Flue Gas using 13X binder free Zeolite: effect of the presence of Sulfur Dioxide

Authors: Celio Cavalcante[1]; Diana Azevedo[1]; Enrique Vilarrasa-Garcia[1]; Eurico Torres[1]; Moises Bastos-Neto[1], Rafaelle Santiago[1]

[1] Universidade Federal do Ceara

Email for correspondence: celio@ufc.br

Carbon dioxide (CO2) capture is a subject of extensive research, particularly with Carbon Capture and Storage (CCS) methods gaining attention, notably those based on gas-solid adsorption. However, there is a notable gap in the literature concerning the impact of contaminants present in gaseous streams, particularly sulfur and nitrogen oxides, on CO2 adsorption. This study evaluated the ef- fect of sulfur dioxide (SO2) presence in gas streams on the performance of CO2 adsorbents using a commercial Köstrolith 13X binder free (13XBF) zeolite (Chemiewerk Bad Köstritz GmbH ,Germany), with a magnetic suspension balance (Rubotherm, Germany) [1].

Before and after exposure to SO2, the 13XBF zeolite underwent physical and chemical characterizations. N2 adsorption/desorption isotherms at 77K revealed a decrease in the amount of adsorbed N2 post-SO2 exposure, while the isotherm shape remained consistent, indicating a type I isotherm according to the IUPAC classification [2]. The decrease in textural properties post-SO2 exposure was attributed to the irreversible adsorption of sulfur species, confirmed through elemental analysis and X-ray photoelectron spectroscopy. The S2p spectrum for 13XBF zeolite after SO2 exposure displayed peaks corresponding to elemental sulfur and sulfate ions, whereas no sulfur species were evident on the zeolite surface before SO2 exposure. Even at low partial pressures (0.045 bar) and constant flow, exposure to SO2 led to irreversible adsorption, with residual SO2 adsorbed even after thermal regeneration under typical zeolite degassing conditions (300 °C in vacuum for 10 hours). This residual SO2 caused a reduction in CO2 adsorption at 0.15 bar across the studied temperature range.

In any cyclic adsorption process, whether thermal swing adsorption (TSA) or pressure swing adsorption (PSA), it is crucial to assess the adsorbent behavior through several adsorption/desorption cycles. After the initial SO2 exposure, a ~35% decrease in CO2 adsorption capacity was observed. However, in subsequent adsorption/desorption cycles, the CO2 adsorption capacity remained essentially constant over 10 cycles.

References:
1. Dreisbach, F et al., Highest Pressure Adsorption Equilibria Data: Measurement with Magnetic Suspension Balance and Analysis with a New Adsorbent/Adsorbate-Volume, Adsorption, 8 (2002), 95–109.
2. M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure and Applied Chemistry, 87 (2015) 1051-1069.

Acknowledgements:
The authors gratefully acknowledge support of RCGI/USP, sponsored by FAPESP (2014/50279-4 and 2020/15230-5) and Shell Brasil, and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.

A Comparative Study of Physical and Chemical Modification for Improved CO2 Capture in Fixed-Bed Adsorption

Suravit Naksusuk[1]

[1] School of Chemical Engineering, Suranaree University of Technology

Email for correspondence: suravit@sut.ac.th

Adsorption is a promising technique for CO2 capture, and improving adsorbent properties is cru- cial for enhancing CO2 selectivity. This study compares the efficiency and differences between two modification methods: physical treatment to increase mesopore volume and active sites, and chemical impregnation with triethylamine (TEA) for CO2 capture in a fixed-bed adsorption system. N2 isotherm analysis revealed an increase in mesopore volume for physically treated activated carbon. Conversely, BET surface area decreased for chemically impregnated samples with increasing TEA concentration, compared to the original activated carbon. Fixed-bed adsorption experiments demonstrated increased CO2 uptake with TEA-impregnated activated carbon, while physically treated carbon exhibited CO2 adsorption capacity similar to the original material. However, diffusivity in the fixed bed remained constant initially, but decreased with increasing TEA concentration due to pore blocking. Despite this, the study identified an approach for enhancing CO2 capture selectivity with a cost-effective preparation method that is scalable for industrial applications and real-world CO2 capture processes.

Analyzing the Performance of Propylamine-Grafted Mesoporous Silica for Direct Air Capture Applications

Amirjavad Ahmadian Hosseini[1] ,Laura Rojas [1]; Masoud Jahandar Lashaki [1]

[1] Florida Atlantic University
Emails for correspondence: mjahandarlashaki@fau.edu, lrojas2021@fau.edu,
aahmadianhos2021@fau.edu

The development of adsorbent materials for CO2 capture from the atmosphere is the focus of this study. There is a widespread agreement among scientists that greenhouse gases (GHGs) are responsible for trapping heat in the atmosphere. The concentration of CO2 in the atmosphere grew from 320 to 425 parts per million by volume (ppmv) between 1960 and 2024. According to NASA, this rise contributed to the 1.2 °C increase in average world temperature compared to the average of the late-19th century. In 2018, the Intergovernmental Panel on Climate Change (IPCC) called for a reduction of 45% in CO2 emissions by 2030, relative to the levels in 2010, to limit the global temperature increase to 1.5 °C. The Blue Map Scenario developed by the International Energy Agency (IEA) suggests various methods to reduce CO2 emissions. These strategies include shifting to renewable energy sources and putting CO2 capture technologies into action. However, most CO2 capture studies have been focused on large point sources such as power plants that run on fossil fuels. CO2 capture from the air, also recognized as direct air capture (DAC), has recently received increased attention. The United States Department of Energy acknowledges the significant contribution that DAC can make in resolving the climate challenge and moving toward the goal of reaching net-zero emissions by the year 2050. Due to their superior performance, DAC applications involving cyclic adsorption-desorption of CO2 by amine-functionalized silica materials (also known as “aminosilica”) have received great attention from both the scientific community and industry. Most relevant research concentrates on near-equilibrium CO2 adsorption while adsorbent stability and adsorption kinetics are considered secondary factors in many studies. While the stability of aminosilicas determines their operational lifetime, it is vital to have fast adsorption kinetics to increase the amount of CO2 captured over a given time. This study aims to employ a novel approach by emphasizing adsorbent stability and rapid adsorption kinetics more than adsorption uptake to create aminosilicas that are highly effective and long-lasting in DAC applications. Aminosilicas were synthesized by utilizing mesoporous silica that is commercially available (CARiACT G-10, Fuji Silycia). The amine functionalization of silica was completed via grafting instead of impregnation to enhance adsorption kinetics and long-term stability of the adsorbent. Amine grafting was conducted using isolated primary amines (i.e., 3-aminopropyltrimethoxysilane; APTMS). Thermogravimetric analysis (TGA) was performed on all the materials to quantify amine loading, equilibrium CO2 uptake, amine efficiency, and CO2 adsorption kinetics in the presence of dry CO2 (400 ppmv, balance nitrogen) at an adsorption temperature of 25 °C. Selected performant materials were further investigated regarding cyclic adsorption-desorption performance, long-term thermal and oxidation stability, and column-breakthrough experiments in the presence of dry and humid gas streams. Our preliminary results indicated that propylamine-grafted silica materials achieved a delicate balance between enhancing CO2 uptake, improving adsorption kinetics, and securing thermal and oxidation stability.

Triamine-Grafted Mesoporous Silica Materials for CO2 Capture from the Atmosphere

Laura Rojas[1] , Amirjavad Ahmadian Hosseini [1]; Masoud Jahandar Lashaki [1]

[1] Florida Atlantic University
Emails for correspondence: mjahandarlashaki@fau.edu, lrojas2021@fau.edu,
aahmadianhos2021@fau.edu

The concentration of CO2, the primary anthropogenic greenhouse gas (GHG) responsible for global warming and climate change, has experienced a rapid increase since the Industrial Revolution. The present levels of CO2 surpass any recorded in human history, indicating a global average concentration of 425 parts per million by volume (ppmv) in 2024, as opposed to 315 ppmv in 1958. Additionally, there is a potential for it to reach 800 ppmv if multifaceted solutions are not implemented. This in- crease in emissions has caused a nearly 2-degree Fahrenheit rise in global temperatures since the pre-industrial era. CO2 capture from the atmosphere, also known as direct air capture (DAC), might help us address this problem. The U.S. Department of Energy has endorsed DAC as one of the help- ful strategies to achieve net-zero emissions by 2050. Owing to their superior performance, DAC applications involving cyclic adsorption-desorption of CO2 by amine-modified silica materials (i.e., "aminosilica") have gained momentum in recent years. These technologies have achieved significant attention because of their potential for commercialization and positive environmental impact to miti- gate climate change. To that end, this project aims to develop materials suitable for DAC applications. This research involves the synthesis of triamine-grafted silica adsorbent materials. Triaminosilane was chosen for this purpose because it possesses two secondary amines and one primary amine, providing a high affinity for CO2 capture. CARiACT G-10 silica (Fuji Silysia Chemical Ltd.) was used as support for the synthesis of aminosilicas. G-10 silica is commercially available at a low cost and has a high pore volume (1.2 cm3/g), large surface area (300 m2/g), small particle size (5 µm), and wide pores (20 nm), enabling it to attain high amine loadings and CO2 uptakes, without compromis- ing adsorption kinetics. Different materials were produced by implementing the grafting technique and varying factors such as the amount of water and triamine to synthesize unique samples. Using thermogravimetric analysis (TGA), the materials were screened for equilibrium CO2 uptake, amine efficiency, and adsorption kinetics in the presence of dry CO2 (400 ppmv, balance nitrogen) at 25 °C. One best-performing material with the highest CO2 uptake and fastest CO2 adsorption kinetics was chosen for rigorous 50-cycle testing under the above adsorption conditions, followed by regen- eration at 120 °C in the presence of N2. The results indicated stable performance as evidenced by maintaining 99% of the initial CO2 uptake throughout cycling. Using column-breakthrough testing, the performance of the final candidate was also evaluated in the presence of humid CO2, confirming previous reports that humidity boosts the CO2 uptake of amine-modified materials. These results suggest the high potential of aminosilicas for DAC applications.

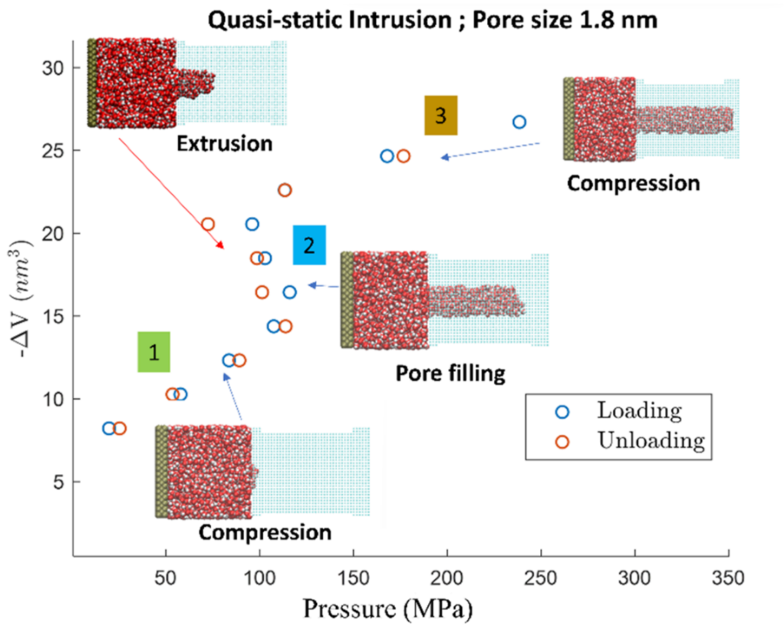
CPM9 | POSTER PRESENTATION
CATEGORY: SIMULATION / THEORY

Molecular mechanisms of water intrusion and extrusion in hydrophobic nanopores

Abdelraheem Abdella[1]; Kolattukudy P. Santo[1]; Alexander Neimark[1]

[1] Rutgers, The State University of New Jersey
Emails for correspondence: santotheophys@gmail.com, aneimark@rutgers.edu

Lyophobic nanoporous particle suspensions are being explored as promising materials for energy absorption and storage. In these systems, known as nanoscale energy absorption systems (NEAS), the non-wetting solvent intrudes into nanopores when subjected to mechanical compression, converting and storing the impact energy that can be further released upon solvent extrusion when the compression force is removed.1 While various NEAS have been explored experimentally, the molecular level mechanisms of the intrusion-extrusion cycles are not well-understood. Using atomistic molecular dynamics simulations (MD), we investigate the dynamics of shock impact induced intrusion and extrusion of water in hydrophobic cylindrical channels. MD simulations performed for nanopores of different sizes at quasi-static and dynamic conditions demonstrate three different stages of the compression process: (1) initial elastic compression of the solvent, (2) fluid intrusion into the pore upon reaching a threshold intrusion pressure and (3) elastic compression of the solvent upon pore-filling (see Fig. 1). Extrusion of the solvent from a completely filled nanopore upon the release of pressure is initiated by the bubble nucleation. Our simulation results are correlated to the experimental observations. (1)



References:

1 Belogorlov, Anton A., et al. "Suspensions of lyophobic nanoporous particles as smart materials for energy absorption." Journal of Colloid and Interface Science 600 (2021): 229-242.

Molecular simulation of separation of C60 and coronene in silica

György Hantal [1]; Ana-Sunčana Smith [2]

[1] PULS Group, Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute for Theoretical Physics, Interdisciplinary Center for Nanostructured Films (IZNF)

[2] 1-PULS Group, Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute for Theoretical Physics, Interdisci- plinary Center for Nanostructured Films (IZNF), 2- Division of Physical Chemistry, Ruđer Bošković Institute

Emails for correspondence: gyorgy.hantal@fau.de, rustam.durdyyev@fau.de, smith@physik.uni-erlangen.de

Classical liquid chromatography is one of the most used techniques in the field of nanoparticle separation. This is achieved by driving the nanoparticle containing liquid through a column densely packed with meso- and nanoporous particles. Separation efficiency can be improved through optimizing the interactions between the particles, the solvent and the pore surface using directed surface modifications or adjusting the solvent composition. Finding the best combination of solvents and functionalized surfaces is a complex optimization problem, which is often aided with molecular dynamics (MD) simulations. In this study, the diffusive transport of model nanonparticles, C 60 fullerene and coronene was studied in nanoconfinement using molecular modeling. The MD simulations were carried out in a slit nanopore of fixed width made of crystalline, fully hydroxylated silica. As solvents, n-hexane and toluene mixtures of different compositions were used. Nanoparticle diffusivities computed both in the bulk and at the surface were used in our 2-state diffusion model to determine the solvent-dependent effective diffusivities of nanoparticles [1]. Our results help to rationalize the observed experimental retention time trends measured for C60 and coronene.

1. Andreas Baer, Paolo Malgaretti, Malte Kaspereit, Jens Harting, Ana-Sunčana Smith, Modelling diffusive transport of particles interacting with slit nanopore walls: The case of fullerenes in toluene filled alumina pores, vol 368, 2022, 0167-7322

Composite Boron Nitride-based Immobilized Nanohydride Toward Self-Accelerated Reversible Hydrogen Storage

Maxwell Tsipoaka[1]; Fateme Rezaei[1]

[1] Missouri University of Science and Technology

Emails for correspondence: mtbr5@mst.edu, rezaeif@mst.edu

Metal hydrides for on-board hydrogen storage play a key role in future conversion of the world to a "hydrogen economy". Nano-structuring these materials proves an effective strategy which can simultaneously enhance their ab/de-sorption thermodynamics and kinetics. However, strategies to combine catalysis and nanoconfinement for controlling factors governing their interfacial hydrogen uptake and release processes are still lacking. In this study, we show how thermal emitting method can be used for generating Mo2N sites to create electron-deficient boron and N-vacancies in inert boron nitride host for LiBH4 activation. The generated Mo2N sites resulted in a shift of the electronic band structure of the host which weakened the Li-B bond of nanostructured LiBH4 species. We demonstrate the tailoring of a strong Mo2N–DBN hybrid structure and clarify the mechanistic origin of its activity. Both experimental results and DFT investigations indicate a long-range interaction of Li in the immobilized nanohydride with B atoms, which optimizes the adsorption energy for absent LiBH4 phase transition and melting upon cycling. This study provides an approach to finely control the host–guest nanointerface interactions of metal borohydride and scaffolds at the atomic level and is expected to guide smart thermodynamic or kinetic alteration of solid-state hydride materials.

Keywords: Density functional theory, Hydrogen economy, adsorption, storage, interfacial charge transfer, nanointerface interactions, electronic band structure, nanoconfinement, thermodynamic or kinetic alteration.

Mechanical Properties of Gases Adsorbed in Micropores from the Fluctuation Theory

Santiago Flores Roman[1], Alina Emelianova [2]; Gennady Gor [3]

[1] New Jersey Institute of Technology

[2] Princeton University
[3] Princeton University, NJIT

Emails for correspondence: saf5@njit.edu, ae3301@princeton.edu, gor@njit.edu

Fluids exhibit different thermodynamic properties in confinement compared to their bulk state. Their boiling and melting temperatures shift, their densities are lower than their bulk phase, and their mechanical properties, such as the elastic modulus, alter depending on the pore size [1]. These phenomena have been analyzed previously through computational models, such as molecular simulations, although the focus on understanding the altered mechanical properties in confinement has primarily centered on mesopores rather than micropores. There were previously only several attempts to study such effects in micropores, including Dobrzanski et al. [2], who analyzed how variations in pore geometry and size influence the mechanical properties of fluids confined in micropores. However, due to the distribution of fluid molecules, when confined in a micropore, being far from the normal distribution, these studies presented a challenge for applying a fluctuation theory to calculate the mechanical properties of a fluid through molecular simulations.

In this work, we studied the elastic properties of nitrogen and carbon dioxide adsorbed in micropores. As a model system, we focused on a recent molecular simulation study of gas adsorption in LTA4A and NaX zeolites [3]. We extended the results obtained in [3] by calculating the mechanical properties of adsorbed nitrogen and carbon dioxide using the fluctuation theory. We found that the enhancement of the elastic modulus is observed in micropores, even when the densities of the adsorbed fluid are lower than in the bulk phase. We concluded that this effect is due to reduced fluctuations in the adsorption of the fluid. We showed that similar calculations can be applied to any fluid adsorbed in a micropore. Therefore, our results bring a deeper insight into the characterization of confined fluids in micropores.

References:
1. C.D. Dobrzanski, B. Gurevich, G. Y. Gor, Elastic Properties of Confined Fluids from Molecular Modeling to Ultrasonic Experiments on Porous Solids, Applied Physics Reviews, 8 (2021) 021317.
2. C.D. Dobrzanski, M. A. Maximov, G. Y. Gor, Effect of Pore Geometry on the Compressibility of a Confined Simple Fluid, The Journal of Chemical Physics, 148 (2018) 054503.
3. A. Emelianova, C. Balzer, G. Reichenauer, G. Y. Gor, Adsorption-Induced Deformation of Zeolites 4A and 13X: Experimental and Molecular Simulation Study, Langmuir, 39(2023) 11388-11397.

The Effect of Carbon Nanotube Diameter on Hydration of Critical Material Ions from E-waste

Qing Shao[1]; Zachary Baker[1]

[1] University of Kentucky
Emails for correspondence: zdba227@uky.edu, qshao@uky.edu

Critical materials such as lithium, nickel, and cobalt play an important role in the sustainable development of society. However, establishing a reliable supply of these critical materials has been a challenge for the USA. Meanwhile, electronic waste (E-waste) has become a societal burden due to the quick spread of electronic devices and electric cars. E-waste contains a large amount of ex- posed lithium, nickel, and cobalt, which will pollute the soil and water if not disposed of properly. Thus, highly efficient technology that can recover critical materials from E-waste can help reduce the detrimental effects of E-waste on the environment and resolve the supply chain issue for those critical materials. One challenge of recovering critical materials from E-waste is developing a separation technology that can differentiate between the materials themselves. Nanoporous materials have shown their exceptional potential in separating substrates with similar chemical and physical features. However, the creation of such nanoporous materials must be based on a full understanding of the molecular thermodynamics of ionic hydration within nanoscale confinement. This work investigates the hydration structure and dynamics of three critical material ions for lithium-ion batteries (Li2+, Ni2+, and Co2+) within carbon nanotubes with a diameter from 1.0-2.0 nm using molecular simulations. We deploy classical and ab initio molecular dynamics (MD) simulations to investigate the structural and dynamic properties of water molecules with those ions within the carbon nanotubes. We also explore the development of deep learning force fields that enable us to investigate the ionic hydration within carbon nanotubes as accurately as ab initio MD simulations, but much faster. The simulation-revealed deviation will be used to develop membrane-based separation technology for recovering critical materials.

Molecular Simulation of Adsorption of Sarin and Simulants on Metal–Organic Frameworks

Elizaveta Basharova[1] , Alina Emelianova [2]; Allen Reed [1]; Gennady Gor [3]; Andrei Kolesnikov [4]

[1] NJIT

[2] Princeton University
[3] Princeton University, NJIT
[4] Department of Chemical and Materials Engineering, New Jersey Institute of Technology

Emails for correspondence: eb374@njit.edu, afr3@njit.edu, ae3301@princeton.edu,
kolesnik@njit.edu, gor@njit.edu

Even in 21st century, chemical warfare agents (CWA) remain a threat, and a lot of research and development is aiming to advance protection from CWA. Experiments with CWAs are dangerous and are typically reduced to a minimum. Most of experiments are done on simulants –chemicals which have similar structure, but much lower toxicity. For sarin simulants include dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), and diisopropyl fluorophosphate (DIFP). Unlike experimental work, molecular simulations are not constrained with the toxicity, so in addition to studies of simulants, simulations can be used for studies of the agents themselves.

In this work we focused on promising adsorbent materials for CWA protection – MOFs - metal-organic frameworks. MOFs are highly porous materials and some of them show strong capacity to capture sarin [1]. We used the selected MOFs from the recent screening study [1] and performed Monte Carlo simulations on adsorption of sarin and its simulants. Although sarin and its simulants have close thermodynamic properties [2], their adsorption behavior can be different, and requires a detailed computational verification. The calculated adsorption isotherms, enthalpy of adsorption and radial distribution functions (RDF) allowed us to select the best MOF for capturing sarin and reveled how similar the interaction between sarin-MOF and simulant-MOF [3]. Based on the calcu- lated properties we have concluded that among all the simulants DMMP demonstrated the closest behavior to sarin. Thereby the results provide insights in selection of the best simulant to study CWA adsorption on MOF's and synthesis new efficient compounds for capturing of chemical war- fare agents.

References:

1. I.Matito-Martos,P.Z.Moghadam,A.Li,V.Colombo,J.A.Navarro,S.Calero,D.Fairen-Jimenez. (2018). Discovery of an optimal porous crystalline material for the capture of chemical warfare agents. Chemistry of Materials, 30(14), 4571-4579.
2. A.Emelianova, E. Basharova, A.Kolesnikov, E.V. Arribas, E.V. Ivanova, G. Y. Gor, Force Fields for Molecular Modeling of Sarin and its Simulants: DMMP and DIMP. J. Phys. Chem. B; 2021, 125, 4086–4098
3. A.Emelianova, A.Reed, E. Basharova, A. Kolesnikov, G.Y. Gor, Closer Look at Adsorption of Sarin and Simulants on Metal–Organic Frameworks. ACS Appl. Mater. Interfaces 2023, 15, 14, 18559– 18567

A unified approach for bridging the gap between cDFT and equation of state for confined fluids

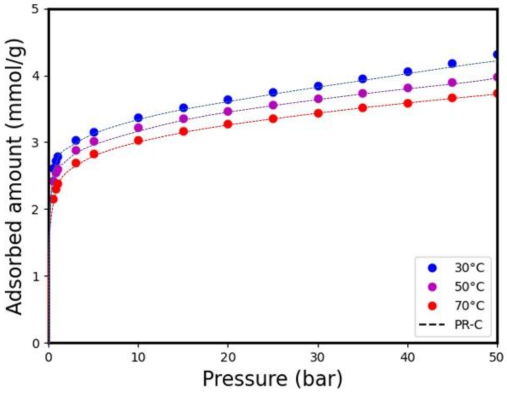
Amaro Gomes Barreto Jr.[1]; Dárley Carrijo de Melo[2]; Felipe Rocha Pinto[1]; Frederico Wanderley Tavares[1]; Vítor Sermoud[3]

[1] Universidade Federal do Rio de Janeiro

[2] CENPES/Petrobras S.A.
[3] Federal University of Rio de Janeiro

Emails for correspondence: amaro@eq.ufrj.br, tavares@eq.ufrj.br, felipefrpinto@gmail.com, darley@petrobras.com.br, vsermoud@gmail.com

In recent years, extensions of the cubic equations of state for fluids confined in different geome- tries have been developed based on the Generalized van der Waals Theory. These equations make it possible to describe the Helmholtz energy as a function of temperature, volume, and number of components, from which expressions for all other thermodynamic properties can be derived. Extending the Equation of States to represent confined fluids in micro and mesopores is still challenging. Although different authors have modified classical expressions like Peng-Robinson1 to model ad- sorption, these models usually reduce the pore structure to simple geometries and pore potentials. Depending on the level of simplification, the methodology can struggle when representing systems in a range of temperatures. Although they have a lower computational cost, they still do not have the robustness seen in methods such as Monte Carlo (MC) simulations or those based on the classical density functional theory (NLDFT). However, MC and NLDFT are the most recommended for micro and mesopores, but it is challenging to use them to obtain thermodynamic properties for fluids in larger pores, generating a demand for a single methodology that covers all scales. Therefore, this work simulates pore confinement with an NLDFT model and uses the fluid physicochemical proper- ties to feed the Peng-Robinson extended to represent the confinement effect. To verify the success of this approach, we carried out CO2 adsorption isotherms on faujasite zeolite in a magnetic suspen- sion balance (Rubotherm) over a pressure range of up to 50 bar. The results show that when we feed this NLDFT information into the equation of state for a confined fluid, the resulting model can more adequately represent the CO2 isotherms in faujasite at different temperatures (Figure).



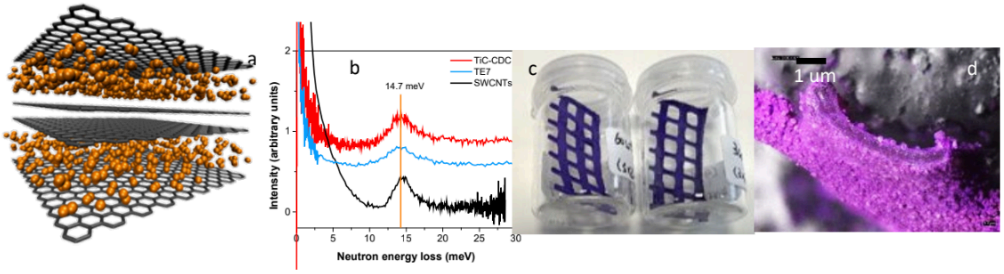
Hydrogen storage: predicting at room temperature in a series of activated carbons

José Carlos Alexandre de Oliveira[1] , Daniel V. Gonçalves [1]; Sebastião M. P. Lucena [1]

[1] Universidade Federal do Ceara
Emails for correspondence: danieldvg@live.com, lucena@ufc.br, jcadeoliveira1@gmail.com

Fuel cell vehicles hold significant promise for decreasing both energy consumption and carbon dioxide emissions. Hydrogen storage is the key technology towards the hydrogen society [1]. Vehicular hydrogen has been stored in special tanks at very high pressures (700 bar) with obvious disadvantages in the energy cost of compression and safety. The use of adsorbed H2 instead of compressed H2 can be a solution to enable safer and more economical storage. Conducting experimental studies of H2 adsorption at high pressures may present operational difficulties and risks. In this study we propose the prediction of H2 adsorption up to 700 bar using the Monte Carlo algorithm in the grand canonical ensemble and the representative pores method that we applied previously in the prediction of isotherms of C1 to C4 [2], H2S [3,4]. Based in that methodology, we predict the adsorption capacity of H2 at 298K between 0.8 to 700 bar on different commercial carbons using textural information of N2 at 77K and CO2 at 273K. At pressures up to 100bar we obtained a good agreement with the experimental data available.

The samples ACC10 and WKL20 have considerable volumes of pores concentrated in the region of well-defined micropores and show a maximum adsorption at 240 bar. The samples ACC15 and ACC20, which have pore volumes in the mesopore region, reach maximum adsorption at pressure of 190. The ACC20 sample presents the highest adsorption amount of 3.15 mmol/g. Among the simulated isotherms of figures 5 and 6, we highlight the carbon Maxsorb, the best result after that presented by carbon ACC20, with 2.96 mmol/g at 130 bar. The Maxsorb sample has simultaneously high volumes in the micro and mesopore regions. This means that an activated carbon that has well- developed regions of microporosity and mesoporosity will have considerable adsorption capacity at relatively small pressures. It was possible to determine the maximum pressure where the highest adsorption of H2 occurs at 298 K with emphasis on Maxsorb that reached 6.14 wt % at 700 bar, near the US Department of Energy (DOE) target value of 6.5 wt.% .



References:
1. Mori D, Hirose K. Recent challenges of hydrogen storage technologies for fuel cell vehicles. Int J Hydrogen Energy (2009) 34:4569–4574. doi:10.1016/j.ijhydene.2008.07.115
2. Lucena SMP, Gomes V a., Gonçalves D V., Mileo PGM, Silvino PFG. Molecular simulation of the accumulation of alkanes from natural gas in carbonaceous materials. Carbon N Y (2013) 61:624–632. doi:10.1016/j.carbon.2013.05.046
3. Gonçalves D V., Paiva MAG, Oliveira JCA, Bastos-Neto M, Lucena SMP. Prediction of the monocomponent adsorption of H2S and mixtures with CO2 and CH4 on activated carbons. Colloids Surfaces A Physicochem Eng Asp (2018) 559:342–350. doi:10.1016/j.colsurfa.2018.09.082
4. Menezes RLCB, Moura KO, De Lucena SMP, Azevedo DCS, Bastos-Neto M. Insights on the Mechanisms of H2S Retention at Low Concentration on Impregnated Carbons. Ind Eng Chem Res (2018) 57:2248–2257. doi:10.1021/acs.iecr.7b03402

Acknowledgements:
The authors wish to acknowledge financial support for this study from CAPES, CNPq and FUNCAP and the use of the computer cluster at National Laboratory of Scientific Computing (LNCC/MCTI, Brazil).

Study of Crystallization Pressure by Molecular Simulation

Authors: Bilal MAHMOUD HAWCHAR^{None}; Laurent brochard^{None}, Florian osselin ; Jean-Michel Pereira ; Matthieu Vandamme ; tulio honorio

Emails for correspondence: laurent.brochard@enpc.fr, tulio.honorio-de-faria@ens-paris-saclay.fr, bilal.mahmoud- hawchar@enpc.fr, matthieu.vandamme@enpc.fr, florian.osselin@cnrs-orleans.fr, jean-michel.pereira@enpc.fr

The in-pore crystallization of salts is considered one of the major sources of degradation of construction materials, geomaterials, and built heritage. When crystallizing, salts may exert mechanical pressure against the surface of the pore, which can damage materials. Crystallization within the porous network remains one of the most misunderstood phenomena in porous media mechanics. We propose an investigation combining molecular simulations and theoretical development to quantify and clarify the origin of the crystallization pressure at the finest scale.

At thermodynamic equilibrium, crystallization pressure results from the change in the solubility of a crystal as it is compressed. Direct molecular dynamics simulations to compute the solubility of salts are challenging because the time scale of dissolution and precipitation, microseconds or more, is at the limit or beyond computing capabilities. For this reason, we use a thermodynamic integra- tion approach to overcome this issue. With this approach, we can quantify the effect of stress on NaCl solubility, and more specifically the effect of stress anisotropy which has been disregarded so far. We use these results to revisit the existing theory describing crystallization pressure and extend it to account for stress anisotropy. After investigating the case of bulk crystallization, we focus on the effect of confinement by looking at the thermodynamics of a salt solution confined in a nanometric thin film at the interface between two crystals. We conduct molecular simulations to determine how the thickness of the film decreases with the normal pressure exerted by the surrounding crystals. Doing so, we identify the critical pressure threshold at which this wetting film, responsible for the crystal growth, will disappear, providing an upper bound to the crystallization pressure phenomenon.

Incorporating material flexibility effects into adsorption modeling using non-local Density Functional Theory

Christelle Miqueu,[1]Raphael Labeyrie

[1] Université de Pau et des Pays de l'Adour

Email for correspondence: cmiqueu64@gmail.com

Among theoretical developments, the molecular density functional theory (DFT) has emerged as one of the most powerful and convenient molecular approach for the description of the thermodynamic properties of inhomogeneous fluids. The development of DFT for classical fluids originates in the late 70's [1] and its use is nowadays widespread for the description of fluid interfaces or flu- ids confined in nanopores, the characterization of porous materials [2], etc. The success of DFT approaches is explained by the fact that they preserve detailed information on the microstructure of inhomogeneous fluids but with a much lower computational expense than molecular simulations. Much progress has been made in recent years in the development of both: i) the formulation of more realistic free energy functionals, necessary to account for complex fluids [3], ii) and more efficient numerical algorithms to apply DFT to complex geometries [4]. DFT framework is naturally derived in the Grand Canonical ensemble, which is suitable for fluid adsorption in rigid frameworks while the appropriate thermodynamic ensemble for the treatment of adsorption in flexible porous mate- rials is the osmotic statistical ensemble. Hence, only a very limited number of DFT-based studies addressed the flexibility of the porous network [5,6]. Few years ago, Coudert et al. [7] proposed a simplification of the osmotic configurational partition function leading to a tractable formulation of the osmotic potential to study the adsorption in flexible porous materials with molecular simulations. In this work, we use this strategy to address the adsorption of fluids in breathing adsorbents with a NLDFT framework. In particular, the adsorption in a material presenting two distinct shapes (large-pore and narrow-pore) is investigated as a representative example of breathing metal-organic framework (such as MIL-53).

Modeling Adsorption of Simple Fluids and Alkanes on 3D Nanoporous Carbons

Nicholas Corrente[1]; Elizabeth Hinks[1]; Aastha Kasera[1]; Raleigh Gough[1]; Peter I. Ravikovitch[2]; Alexander Neimark[1]

[1] Rutgers University, New Jersey, USA
[2] ExxonMobil Research and Engineering Company

Emails for correspondence: peter.ravikovitch@exxonmobil.com, cpm9.admin@rutgers.edu, aneimark@rutgers.edu

Predicting adsorption on nanoporous carbonaceous materials is important for developing various adsorption and membrane separations, as well as for oil and gas recovery from shale reservoirs. Here, we explore the capabilities of 3D molecular models of disordered carbon structures to reproduce the morphological and adsorption features of practical adsorbents. Using grand canonical Monte Carlo simulations, we construct a series of adsorption isotherms of simple fluids (CO2, N2, and SO2) and a series of alkanes from methane to hexane on two model 3D structures: purely microporous structure A and micro-mesoporous structure B. We show that structure A reproduces the morphological properties of commercial Norit R1 Extra activated carbon and demonstrates outstanding agreement between the simulated and experimental adsorption isotherms reported in the literature for all ad- sorbates considered. Good agreement is also found for simulated and measured isosteric heats. This work provides a new insight into the specifics of structural and adsorption properties of nanoporous carbons and demonstrates the advantages of using 3D molecular models for predicting adsorption hydrocarbons and other chemicals by MC simulations.

This work is supported by the NSF CBET grant 1834339 and ExxonMobil.

N.J. Corrente, E.L. Hinks, A. Kasera, R. Gough, P.I. Ravikovitch, A.V. Neimark, Modeling adsorp- tion of simple fluids and hydrocarbons on nanoporous carbons, Carbon 197 (2022) 526-533. DOI: 10.1016/j.carbon.2022.06.071

SAFT-DFT Studies of Nanoporous Carbon Deformation Induced by Multicomponent Adsorption

Nicholas Corrente[1]; Elizabeth Hinks[1]; Aastha Kasera[1]; Alexander Neimark[1]

[1] Rutgers University, New Jersey, USA

Emails for correspondence: cpm9.admin@rutgers.edu, aneimark@rutgers.edu

We consider deformation of nanoporous carbons during adsorption of mixtures, focusing on the specific context of carbon dioxide displacement of natural gas from coal and shale reservoirs. Density functional theory calculations augmented by the perturbed chain statistical associating fluid theory (SAFT-DFT) are employed to model adsorption of fluid mixtures on carbon slit pores at geo- logically relevant temperatures and pressures. The adsorption stress is calculated from the change in the grand thermodynamic potential of the adsorbed fluid with respect to the change in pore volume. Adsorption of methane and carbon dioxide mixtures is studied in pores of various size. We determine the effect of pore size and fluid composition on the adsorption-induced deformation. The results of this method show good agreement with atomistic GCMC simulations at a fraction of the computational cost.

This work is supported by the NSF CBET grant 1834339.

Development and application of an advanced percolation model for pore network characterization by physical adsorption

Jakob Söllner[1]; Alexander Neimark[2]; Matthias Thommes[3]

[1] Institute of Separation Science and Technology, Friedrich-Alexander Universität Erlangen-Nürnberg

[2] Rutgers University, New Jersey, USA
[3] Friedrich-Alexander-University Erlangen-Nürnberg

Emails for correspondence: jakob.soellner@fau.de, aneimark@rutgers.edu

Physical adsorption is one of the most widely used techniques to characterize porous materials because of being reliable and able to assess micro- and mesopores within one approach. However, challenges and open questions persist in characterizing disordered and hierarchically structured porous materials. This study introduces a pore network model aiming to enhance the textural characterization of nanoporous materials. Our model, based on percolation theory on a Bethe lattice, includes all mechanisms known to contribute to adsorption hysteresis in mesoporous pore networks during capillary condensation and evaporation. The model accounts for delayed and initiated condensation during adsorption as well as equilibrium evaporation, pore blocking and cavitation during desorption. Coupled with dedicated non-local-density functional theory (NLDFT) kernels, the proposed method provides a unified framework for modeling the entire experimental adsorption-desorption isotherm, including desorption hysteresis scans. Hence, this model unveils key pore network characteristics like the effective connectivity, but also has the potential to determine pore size distributions of mesoporous materials by taking quantitatively pore network effects into account. The applicability of the method is demonstrated on a selected set of nanoporous silica materials exhibiting distinct types of hysteresis loops (types H1, H2a, H1/H2a and H5), including ordered mesoporous silica networks, i.e, KIT-6 silica, hybrid SBA- 15/MCM-41 silica with plugged pores, but also two disordered silica pore networks, i.e., a hierarchical meso-macroporous monolith and porous Vycor glass. For all materials, good correlation is found between calculated and experimental primary adsorption and desorption isotherms as well as desorption scans allowing for a determination of key pore network characteristics such as pore connectivity and pore size distributions as well as a parameter correlated with the impact of pore network disorder and corresponding effects on the adsorption behavior. The versatility and enriched textural insights provided by the proposed novel network model allows for a comprehensive characterization previously inaccessible, and hence will contribute to a further advancement in the textural characterization of novel nanoporous materials. It has the potential to provide important guidance for the design and selection of porous materi- als for optimizing various applications, including separation processes (such as chromatography), heterogeneous catalysis, gas-and energy storage. [1]