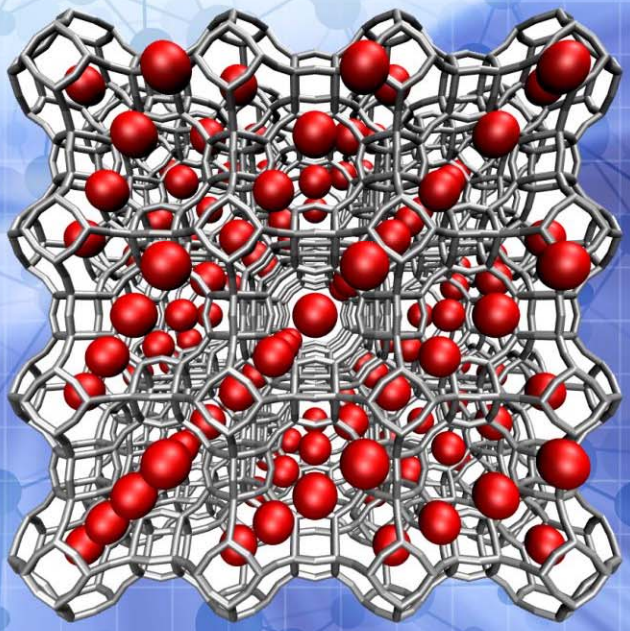
Measurement Needs in the Adsorption Sciences

Workshop Summary Report



April 2015

Prepared by
Energetics Incorporated, Columbia, Maryland
for the

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

and the
Council for Chemical Research

PREFACE

The *Workshop on Measurement Needs in the Adsorption Sciences* was co-sponsored by the Council for Chemical Research (CCR) and National Institute of Standards and Technology (NIST) on November 5–6, 2014, at the NIST Gaithersburg, Maryland campus. The workshop was planned and executed under the direction of workshop co-chairs Matthias Thommes (QuantaChrome Instruments) and Roger van Zee (NIST). The information contained herein is based on the results of the workshop, which was attended by more than fifty experts from government, industry, and academia. The key measurement needs identified and described in this report reflect the expert opinions of workshop participants, but are not intended to represent the views of the entire adsorption sciences community.

Measurement Needs in the Adsorption Sciences

WORKSHOP SUMMARY REPORT

April 2015

Prepared by

Energetics Incorporated, Columbia, Maryland
for the
National Institute of Standards and Technology
and the
Council for Chemical Research

ACKNOWLEDGMENTS

Many thanks to all those who participated in the *Workshop on Measurement Needs in the Adsorption Sciences* held November 5–6, 2014 at the NIST campus in Gaithersburg, Maryland. The presentations and discussions that took place at the workshop provided the foundation for this report. Special thanks are extended to the plenary speakers (listed below) and to the many expert participants (a complete list is provided in Appendix A).

Plenary Speakers

Laura Espinal, *National Institute of Standards and Technology*
Peter Monson, *University of Massachusetts – Amherst*
Alex Neimark, *Rutgers University*
Jim Ritter, *University of South Carolina*
Daniel Siderius, *National Institute of Standards and Technology*
Randy Snurr, *Northwestern University*
Orhan Talu, *Cleveland State University*
Matthias Thommes, *Quantachrome Instruments*
Michael Tsapatsis, *University of Minnesota*
Krista Walton, *Georgia Institute of Technology*
Jennifer Wilcox, *Stanford University*

Special thanks are due to the Energetics Incorporated team who led the workshop planning, facilitation, and preparation of the summary report under the direction of Roger van Zee (NIST). This workshop support team included Melissa Eichner, Ridah Sabouni, Katie Jereza, and Heather Liddell.

Further information about this report can be obtained by contacting Roger van Zee at roger.vanzee@nist.gov.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER 1: INTRODUCTION

OVERVIEW

Adsorption is a surface phenomenon in which molecules or ions from a gas or liquid (the adsorbate) adhere onto a solid surface. The behavior of an adsorptive material is highly dependent on its specific surface area, pore size distribution and pore volume, chemical interactions with the adsorbate, and other factors; therefore, accurate characterization tools are essential to evaluating an adsorptive material's properties and capabilities. Accurate analysis of measured data is essential to ensure that reported results are meaningful and reproducible, while modeling and simulation techniques such as high-throughput molecular screening can accelerate the development of new adsorptive materials. As experimental and analytical techniques become more complex, the consistency of data reported by members of the scientific community has become increasingly important. Therefore, consistent practices in the community—including improved protocols for sample preparation, measurement and data reporting—represent a major cross-cutting research need in this field.

Many key applications for adsorptive materials are related to their capabilities to store and selectively filter fluids and gases. Adsorptive materials could be used to store natural gas or hydrogen fuels in a vehicle, for example, eliminating the need for a high-pressure compressed gas tank. Novel materials such as metal-organic frameworks (MOFs) with high adsorption capacities are under active development for these applications. Adsorptive materials can also be used for separations applications such as water purification, removal of contaminants from pipeline gases, and carbon dioxide capture.

During the *Workshop on Measurement Needs in the Adsorption Sciences*, researchers met to discuss the state of art and identified the key measurement science challenges in this active field. Discussions focused on the important areas of characterization, advanced materials for adsorption applications, and data harmonization. This meeting summary report provides a summary of those discussions.

WORKSHOP SCOPE AND PROCESS

The *Workshop on Measurement Needs in the Adsorption Sciences* was held on November 5–6, 2014 at the National Institute of Standards and Technology (NIST) campus in Gaithersburg, Maryland. It was co-sponsored by the Council for Chemical Research (CCR) as a New Industry and Chemical Engineering (NiChE) workshop. More than fifty adsorption sciences experts from industry, government, the national laboratories, and academia gathered to identify measurement science challenges and associated research and development (R&D) needs in the adsorption sciences.

Specific workshop objectives included:

- Developing a list of the current state-of-art and emerging technologies in the adsorption sciences;
- Prioritizing the most critical measurement needs to advance the science of adsorption; and
- Identifying promising pathways to overcome the major R&D barriers affecting this field today.

An additional focus of the workshop was the newly commissioned Facility for Adsorbent Characterization and Testing (FACT) at NIST's Material Measurement Laboratory (MML). FACT was funded by the Advanced Research Projects Agency-Energy (ARPA-E), and houses state-of-the-art instrumentation for characterizing the gas sorption properties of materials. During the workshop, participants had an opportunity to learn about the new facility and its capabilities and provide input on how the facility might best serve the needs of the adsorption sciences community.

The workshop included four plenary sessions and extended breakout sessions, as described below. The workshop also included a tour of the FACT laboratory. A list of participants is provided in Appendix A and the full workshop agenda in Appendix B.

PLENARY PRESENTATIONS

Presentations from leading experts in the adsorption sciences community set the stage for subsequent discussions in the workshop breakout sessions. Summaries of the presentations are as follows:

- ***Facility for Adsorbent Characterization and Testing (FACT)****: Laura Espinal, NIST*

  Laura Espinal provided an overview of FACTinstruments and measurement capabilities. This newly commissioned facility provides state-of-the-art measurement capabilities for impartial, accurate testing and characterization. Measurement equipment includes volumetric instrumentation, gravimetric instrumentation, and combined systems for multi-component gas mixtures. Adsorptives include carbon dioxide, methane, hydrogen, nitrogen, helium, water vapor, and toluene. The facility also offers high pressure measurements, cryogenic capabilities, and environments for samples sensitive to oxygen. Dr. Espinal noted that a major challenge in adsorptive material characterization is assuring consistent, reliable measurements between laboratories; there are often discrepancies in isotherm data from "round robin" studies. Currently, work is ongoing at FACT to develop credible isotherm data for reference materials to enable reliable comparisons of data between independent laboratories. Three reference materials (Zeolite A [RM-8851], Zeolite Y [RM-8850], and ZSM-5 [RM-8852]) have been extensively characterized for purity, chemical composition, and homogeneity. The lab is now planning a round robin study with the participation of multiple laboratories to compare measurements of carbon dioxide adsorption isotherms across facilities.

- ***The NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials****: Daniel Siderius, NIST*

  Daniel Siderius demonstrated the NIST/ARPA-E *Database of Novel and Emerging Adsorbent Materials*, available online at http://adsorbents.nist.gov. The database, which includes digitized data for 19,628 adsorption isotherms pulled from over 2,500 technical papers, functions as a repository and search engine for adsorbent materials and data about their characteristics—essentially, a "one-stop shop" for data. Comparison of data is enabled through online tools such as isotherm plotting, allowing "virtual" round robin studies. The database can be searched by adsorbent and/or adsorbate name, type of study (e.g., simulation, modeling, or experiment), temperature or pressure range, or publication details. Each database result provides a direct link to the journal article DOI for additional information.

- ***Quenched Solid Density Functional Theory of Adsorption for Heterogeneous Solids and Pore Structure Characterization****: Alex Neimark, Rutgers University*

  Alex Neimark compared the Quenched Solid Density Functional Theory (QSDFT) to the Non-Local Density Functional Theory (NLDFT) for several adsorption situations. NLDFT, the most popular method for pore size characterization, models adsorption in pores with smooth walls. The resulting packing of molecules on the surface creates a layering effect, causing "steps" in the adsorption isotherm that are not observed experimentally. Prof. Neimark noted that *all* non-crystalline adsorbent materials have rough pore walls—even ordered solids like SBA-15 or MCM-41—and that layering defects can become very significant in microporous materials. In contrast, the QSDFT model avoids artificial stepping through a diffused wall model. The result is an absolutely smooth isotherm, which correlates well with experimental results. The model can be applied to spheroidal and cylindrical pores with pore sizes ranging from 0.36 nm (i.e., molecular diameter) to 50 nm. The QSDFT technique can also be used in combination with x-ray diffraction (XRD) for more information about the pore structure and the distribution of fluid in the pores.

- ***Understanding Adsorption/Desorption Hysteresis for Fluids in Mesoporous Materials using Simple Molecular Models and Classical Density Functional Theory****: Peter Monson, University of Massachusetts – Amherst*

  Peter Monson discussed hysteresis behavior using two model systems: a duct pore with a rectangular cross section, and a rectangular ink bottle pore with a larger cross section at the center and narrow "necks." Both pores were open to fluid on both sides. A lattice gas model was adopted to reduce the cost of calculations. Prof. Monson showed that during adsorption in the duct pore, a nucleation process is involved in the creation of the liquid bridge, but during desorption, there is no need to nucleate a liquid bridge; the result is hysteresis. In the ink bottle pore, a wide hysteresis loop results from a bubble that forms in the pore (cavitation). During adsorption, density is built up in the liquid-filled necks before the cavity fills; during desorption, the cavity empties with the necks filled. It was pointed out that in density functional theory (DFT), an assumption of a monotonic relationship between pressure and pore size implies matching adsorption and desorption curves; therefore, non-monotonic assumptions are necessary to produce hysteresis curves.

- ***New IUPAC Recommendations: Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution:*** *Matthias Thommes, QuantaChrome Instruments*

  Matthias Thommes provided an overview of updated International Union of Pure and Applied Chemistry (IUPAC) recommendations on physisorption of gases that will be published in 2015. The new report will update the seminal 1985 report, "Reporting Physisorption Data for Gas/Solid Systems," to reflect 25 years of advances in technology, including the development of tailored pore structures and new experimental challenges. Dr. Thommes remarked on the key updates, including:

  - New classification of pore sizes, including a new subclassification for micropores
  - Updated classification of isotherms and hysteresis, including two new isotherms and two new hysteresis loops
  - New methods for surface area determination for microporous materials (for which Brunauer-Emmett-Teller [BET] theory is insufficient)

- ***The Interplay between Experiment and Simulation for the Design of New Metal–Organic Frameworks****: Randall Snurr, Northwestern University*

  Randall Snurr presented research on the accelerated design of metal–organic frameworks (MOFs) through high-throughput virtual screening. He likened MOFs to "molecular tinker toys" consisting of linker molecules connecting metal–metal oxide nodes. Modeling can therefore be a very useful tool for identifying hypothetical MOFs from a library of building blocks. Prof. Snurr's research group developed the Music code (http://zeolites.cqe.northwestern.edu/Music/) to predict zeolite properties using Monte Carlo simulation. They recently used this method to identify new materials for storage of natural gas. The optimal material would have a large accessible surface area, high free volume, high heat of adsorption, and narrow pore size distribution. Using Music, over 137,000 hypothetical MOFs were screened, and a few hundred were predicted to be better than the current best material for methane storage. In addition to identifying candidate MOFs, high-throughput screening can be used to generate large amounts of data to analyze structure-property relationships.

- ***Understanding the Stability of Metal–Organic Frameworks under Humid Conditions****: Krista Walton, Georgia Institute of Technology*

  Krista Walton discussed the impact of humidity on MOF stability. She noted that this is a relatively new field of study, the first water isotherm having been reported in 2002. Challenges include the large variety of MOFs and that few MOF families can be systematically varied. Further, stability results differ for water vapor and liquid water exposure, and water stability does not necessarily mean water *repellent*. Prof. Walton remarked on some interesting behaviors of MOFs. For one, capillary effects can occur: if water is removed from a porous structure, the structure itself can come apart. In some cases, submersion in solvent can cause the structure to reassemble. MOFs can also exhibit "breathing" behaviors. During assembly in water, narrow pores form; once water is removed, the material "breathes" to form large pores. During cooling, the material reverts to narrow pore form. She noted that MOF stability can be improved by changing functional groups: for example, DABCO MOF (DMOF) is stable to 40% RH, but its stability can be increased by switching 1,4-benzenedicarboxylate (BDC) out for another functional group. Methods for characterizing stability include XRD, Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy, and molecular simulation.

- ***Characterization of Gas Shales for Enhanced Natural Gas Recovery and Carbon Storage Applications****: Jennifer Wilcox, Stanford University*

  Jennifer Wilcox presented research on the characterization of the chemistry and morphology of gas shales. Her work focused on two shale deposits: the Eagle Ford and Barnett shale gas plays. Porosity in shales is provided by clay and kerogen, and she demonstrated that the primary uptake of adsorbed gas occurs in the kerogen. At subsurface conditions (e.g., 80°C), carbon dioxide uptake was found to be enhanced over methane uptake—prompting a research idea that carbon dioxide could potentially be used as a means to extract gas. She noted that idealized synthetic shales differed significantly from real shales in terms of pore size distributions, and commented that this may be a result of poor assumptions in existing models: for example, models assume slit-shaped pores, whereas kerogen pores may be closer to cylindrical. Accurate models may help provide better estimates of shale storage capabilities and the amount of available natural gas.

- ***Two-Dimensional Zeolites for Separation Applications****: Michael Tsapatsis, University of Minnesota*

  Michael Tsapatsis discussed recent developments in the synthesis and characterization of pillared zeolite membranes. Mobil synthesized the first pillared MWW zeolite in 1999, using a process consisting of swelling, pillaring, and calcination steps. In 2012, Prof. Tsapatsis' group developed the first one-step synthesis method for self-pillared zeolite nanosheets. The deactivation behaviors of the pillared mordenite framework inverted (MFI) (Mobil process) and the self-pillared material were similar. The characterization of pore size distributions is difficult because of hierarchical micro- and mesoporosity, with micropores 0.52 nm wide and mesopores 2–7 nm wide. Simulation of adsorption revealed that mostly the micropores are felt at low pressures, whereas the mesopores start to have an impact at higher pressures. In XRD testing, the zeolite nanosheets had the expected diffraction pattern from their in-place crystallinity, despite the sheets being only 2–3 nm thick. In fact, layer thickness could be evaluated using a crystallographic technique: by measuring the extinguishing time for a "dot" in the XRD diffraction pattern, the number of unit cells could be determined. Prof. Tsapatsis concluded by noting that high-performance MFI zeolite membranes represent more than ten to fifteen years of work, but adsorption data are lacking. There is a strong need for small quantity/thin film measurement methods.

- ***Frequency Response: A Powerful Technique for Discerning Gas Phase Diffusional Mechanisms and Rates in Nanoporous Adsorbents****: Jim Ritter, University of South Carolina*

  Jim Ritter began his presentation by remarking on the relative advantages and disadvantages of a number of common methods for determining dominant mass transfer mechanisms and rates, including nitrogen breakthrough, thermogravimetric (TGA) uptake and release, and one-bed rapid pressure swing adsorption (PSA). He showed that time constants differ depending on the technique used—but that accurate values are essential for process modeling. Frequency response techniques were offered as a new strategy. These techniques were demonstrated to consistently and accurately predict mass transfer rates, and can also be used to identify the dominant mass transfer mechanisms at play.

- ***Role of Thermodynamics in Adsorptive Gas Storage Applications****: Orhan Talu, Cleveland State University*

  Orhan Talu discussed challenges in the application of thermodynamics in gas storage applications and pitfalls in conventional data reporting. He noted that the Gibbs definition of surface excess adsorption only defines the reference state but does not specify its properties such as the location of the surface. In microporous materials, the apparent pore density depends strongly on the probe molecule: for example, if a molecule bigger than the pore is used, the pore density will be zero. Pore densities are therefore only meaningful if the probe is specified, e.g., "nitrogen pore density." Thus, pore density is not a property of the solid but of the adsorbent-adsorbate pair. Gibbs definition can be used without any need for a probe molecule to quantify adsorption in net adsorption framework. Net adsorption can also be directly used for adsorptive gas storage. When we make measurements of adsorption, we are actually measuring either; (1) the amount of gas introduced into a volume, or (2) the mass change of a solid. These actual, primary measurements are the net adsorption. In contrast, excess and absolute adsorption values are calculated values based on measurements with other gases as probe. Reported excess/absolute values are then converted back to net adsorption to perform storage calculations. Unless the back-and-forth calculations match exactly, wide discrepancies in the results should be expected for high pressure adsorptive gas storage applications with absolute and excess adsorption.

BREAKOUT SESSIONS OVERVIEW

The breakout sessions focused on three topics: characterization, advanced materials for adsorption applications, and storage and separation applications. Each breakout group responded to the following focus questions:

State of Art (SOA)

- What were the SOA highlights from the plenary presentations?
- What new directions and capabilities are impacting this field?
- What important new trends are taking place in the adsorption sciences?

Challenges and Barriers

- What specific innovations and improvements in measurement science must be addressed?
- What are the major challenges associated with data reporting and comparability of data?
- What are the major standards and reference materials needs?

Figure 1-1. Workshop Topics

- **Characterization** – techniques for the characterization of adsorbent materials, including isotherm measurement/ prediction and pore structure evaluation; experimental and theoretical methods are both covered
- **Advanced Materials for Adsorption Applications** – existing and emerging adsorption applications, such as gas storage and membrane separations, and the design and synthesis of advanced materials for those applications
- **Data Harmonization and Standards** – data reporting protocols, standards for sample preparation and use, and needs for reference materials

Potential Pathways, Solutions, and Approaches

- What solutions/research targets are needed to address the needs and overcome the identified challenges?
- What key metrics/measures of success would show progress towards these solutions/targets over the next five to ten years?

In this summary report, the remarks made by participants have been combined across all breakout sessions and organized topically into major themes, as shown in Figure 1-1. Chapter 2 covers characterization techniques in the adsorption sciences, including both experimental and theoretical methods. Chapter 3 covers advanced applications for adsorptive materials and the associated measurement and synthesis challenges. Chapter 4 covers measurement standards, data reporting protocols, and reference materials. It is noted that two of the workshop breakout groups (Advanced Materials for Adsorption Applications and Storage and Separation Applications) had very similar discussions, both focusing on advanced applications for adsorptive materials and associated measurement needs. In this report, these topics have been combined into a single chapter. Chapter 4 (Data Harmonization) compiles the relevant feedback from all breakout groups on data harmonization, which was identified by all groups as a major overarching challenge in the adsorption sciences.

For each topical area, priorities have been laid out based on the expert feedback of the attendees. These priorities represent some of the most important actions that could be taken to address the current measurement needs in the adsorption sciences.

CHAPTER 2: CHARACTERIZATION

EMERGING TECHNIQUES AND NEW TRENDS

Many advanced measurement methods that have developed in recent years combine multiple independent measurement techniques, such as microscopy and XRD, with conventional adsorption measurement methods. Combined techniques often provide greater insight into material phenomena than would otherwise be possible. *In situ* and *in operando* techniques have also emerged as critical state-of-the-art technologies, allowing researchers to observe "working" adsorbents for improved understanding of material behavior. Further, modeling and simulation studies are recognized as important complements to experimental results. Table 2-1 provides details of emerging characterization techniques and trends identified by workshop participants.

Table 2-1. Emerging Characterization Techniques and New Trends

Emerging Measurement Techniques
• Time-domain NMR, especially for insight into selective adsorption
• Multi-technique and *in situ* approaches, combining adsorption measurements with independent techniques such as XRD and microscopy
• Ultrasonic (electro-acoustic) pore size characterization
• Small angle x-ray scattering
• Dynamics as a tool in characterization
New Trends in Modeling and Theory
• Advances in DFT molecular simulation for improved understanding of basic phenomena
• Modeling and calculations as an important part of investigation (providing a robust complement to measurements)
• Emerging questions regarding fundamentals—e.g., net adsorption (what is being measured?)
• Hysteresis described with new insight using model systems
• Incorporation of fluid–solid interfaces into models

RESEARCH NEEDS AND CHALLENGES

Workshop participants identified materials characterization needs ranging from new experimental measurement capabilities to improved modeling and calculation techniques. Table 2-2 provides further details of identified research needs related to material characterization.

Experimental Needs: The four highest-priority research needs in characterization involved enhanced experimental capability needs. Multi-technique measurement methods are needed to provide a complete picture of adsorption processes, including the adsorption rate, diffusional mechanisms at play, pore structure, and competitive adsorption activity. Therefore, complementary measurement techniques that can work together are needed. Kinetic and diffusion measurement techniques are essential to evaluate non-equilibrium behavior of adsorbents. High-throughput assessment techniques are also a major research need, as the time it takes to make measurements slows the pace of research and limits innovation. Automated techniques could increase the pace by enabling measurements to be made continuously. High-throughput techniques that could quickly screen adsorbent performance could greatly increase the rate at which new materials can be evaluated. Finally, *in situ* and *in operando* studies allow the evaluation of dynamic adsorption, activation, and assembly processes. Improved techniques for *in situ* measurements are needed to advance research in this area.

Lower-priority experimental needs include techniques for measuring heat of adsorption and heat capacities, measuring macropore volume distribution, and making surface area and pore volume distribution measurements

on wetted samples. The availability of "real" inert devices and carrier/tracer molecules could help to improve existing experimental techniques. Measurement capabilities are also needed for very small quantities of material. There is also interest in quantifying the effect of trace impurities on adsorption measurements.

Modeling and Theory Needs: Participants recognized a need to improve modeling of experimental results. A standard DFT code for pore size analysis would enable consistent calculation. Further, there is a need for calculations to be more accessible to non-experts; incorrect calculations in the literature are prevalent.

Table 2-2. Research Needs for Characterization of Adsorptive Materials
(● = one vote)

Experimental Needs	
First Tier Priority	• Identify complementary independent/multi-technique measurement techniques ●●●●●●● • Develop techniques for measuring kinetics and diffusion ●●●●●●●● • Develop protocols and devices for rapid assessment of adsorbent performance (less time and high throughput) ●●●●●● • Develop *in situ* and *in operando* adsorption measurement techniques to characterize "working" adsorbents ●●●●●●
Second Tier Priority	• Develop method for measuring heat of adsorption ● • Develop method for determining volume/density of adsorbent ●
Third Tier Priority	• Develop new methods for macropore volume distribution measurements • Automate measurements to increase the pace of research • Develop method for distinguishing between cavitation/over-compression hysteresis and swelling-related hysteresis • Make "real" inert devices available for measurements • Develop method for measuring heat capacities on microporous materials • Quantify effect of trace impurities on measurements • Develop capabilities to measure very small quantities of material • Improve understanding of adsorbent stability and degradation during reactivation/regeneration • Develop method to make surface area and pore volume distribution (PVD) determinations for "wetted samples" that would change under vacuum • Make carrier or tracer molecules available to use in measurements
Modeling and Theory Needs	
Second Tier Priority	• Develop standard DFT codes for pore size analysis ●● • Improve modeling of experimental results ●
Third Tier Priority	• Increase accessibility of calculations to non-experts • Compare simulations to absolute for helium measurements for hydrogen (low capacities and uptakes) • Improve understanding of thermodynamics in fluid/porous materials

POTENTIAL SOLUTIONS AND APPROACHES

Solutions were identified to address the top four characterization challenges:

Complementary Independent Measurement Techniques: Independent techniques could include XRD, small-angle scattering techniques, 3-D tomography, microscopy, and modeling studies. Researchers could partner with state-of-the-art imaging facilities to correlate adsorption studies with imaging studies. Specific emerging materials, such as shales, could point to unique measurement approaches; multi-technique methods specific to important applications could be explored explicitly.

Measurement Methods for Kinetics and Diffusion: Methods well suited to kinetic studies include manometric systems, calorimetry, coupled volume uptake, and NMR. Non-equilibrium data collected during "equilibrium" adsorption measurements could be used for adsorption studies. A standard kinetic measurement technique—i.e., an IUPAC recommendation or similar—could promote consistency and advance this field. Calculations can be complicated for kinetics, so it is important that researchers publish their original measurements so that their data and assumptions are understood.

High-Throughput Assessment Techniques: Non-traditional methods could be used as rapid-throughput screening tools. It may help to focus on specific applications, such as low-pressure separations or high-pressure storage. Ideally, it would be possible to predict an entire isotherm curve from just a few data points.

In Situ Measurement Techniques: *In situ* and *in operando* studies should be done in relevant industrial conditions. To maximize effectiveness, the range of techniques that are most relevant should be identified simultaneously and integrated into the unit *in situ*.

Further details of the approaches are provided in Table 2-3.

Table 2-3. Potential Solutions and Approaches to Address Needs

Independent/Multi-Technique Measurement Methods
• Partner with state-of-the-art imaging facilities to correlate adsorption studies with imaging studies • Develop a multi-technique approach to characterize gas adsorption, including studies at different pore-diameter length scales (at NIST or a third-party independent laboratory) • Focus on techniques specific to new/emerging materials, such as geologic materials, that present unique challenges • Independent techniques for characterizing adsorption could include: – XRD – Small angle scattering techniques – 3-D tomography – Microscopy – Modeling studies
Kinetics and Diffusion Measurements
• Utilize non-equilibrium data collected during "equilibrium" adsorption measurements for kinetics studies • Develop protocols for analyzing adsorption kinetics from manometric systems and other breakthrough systems suited to kinetic studies • Perform kinetic studies via calorimetry, coupled volume uptake, and NMR at high pressure • Develop automated and rapid measurement techniques for binary equilibrium and kinetics • Standardize kinetic measurement techniques (as IUPAC recommendations do) • Publish original measurements (calculations can be complicated for kinetics)

Table 2-3. Potential Solutions and Approaches to Address Needs

Accelerated Adsorption Devices and Protocols

- Explore non-traditional measurements as screening tools
- Develop ability to predict isotherm from a few data points
- Focus on specific applications: e.g., low-pressure separations and high-pressure storage
- Measure gas density, e.g., binary mixtures
- Metrics for success:
  - High throughput, e.g., 50 samples/day (one adsorption point) with enough accuracy for use as a screening tool
  - Portability of device for industrial use

In Situ and *In Operando* Measurements

- Simultaneously define the range of techniques that are the most relevant (infrared [IR] spectroscopy, multiple internal reflection [MIR] spectroscopy, etc.) and integrate these into the unit *in situ*
- Perform testing in industrially relevant conditions
- Metrics for success:
  - Appropriate particle morphologies
  - Stability targets met

CHAPTER 3: ADVANCED MATERIALS FOR ADSORPTION APPLICATIONS

EMERGING APPLICATIONS AND NEW TRENDS

A wide variety of emerging adsorption applications were identified, ranging from radioactive material clean-up to drug delivery. Many of the applications focused on the capabilities of adsorbent materials in storage and separations. New trends include the use of zeolites as catalysts, such as in the catalytic cracking of gas oil, and site-specific adsorption. The MOF material PCN-14 emerged several years ago as a material with extremely high methane storage capacity. Experimentation has been ongoing since to better characterize this material and its potential capabilities, and to identify MOF materials with even higher capacities. Research has also focused on ordered porous carbon materials for electrochemical energy storage in recent years. Finally, there has been increasing interest in studying the adsorption properties of high-molecular weight oil shales. Table 3-1 provides an overview of emerging applications and trends.

Table 3-1. Emerging Applications and New Trends

Emerging Adsorption Applications
• High-capacity adsorbents for CO_2 separation • Adsorption of contaminants in hydrofracturing wastewater (e.g., biochar) • Biogas purification (to reach pipeline quality) • Purification of petrochemical and refinery steams (e.g., removal of sulfur compounds, nitrogen compounds, oxygenates) • Air purification and clean-up (e.g., removal of organics, carbon monoxide, and small particles) • Energy storage and energy conversion • Drug delivery • Adsorption heat pumps and refrigerators • Gas and vapor sensing (e.g., hydrogen sensing) • Radioactive material clean-up
New Trends in Advanced Materials for Adsorption Applications
• Catalysts, e.g., for mixed hydrocarbons and catalysis for zeolite/oxide systems • Site-specific adsorption of carbon dioxide and other gases in nanoporous materials • PCN-14 for methane storage (static capacity) • MOFs in storage and separation applications • Ordered carbon materials for electrochemical applications • Focus on shale oils (rather than shale solids) and high molecular weight adsorption chemistry

RESEARCH NEEDS AND CHALLENGES

Workshop participants identified several challenges associated with materials development and adsorption applications. Table 3-2 provides further details of the key research needs identified.

Metal–Organic Framework Needs: Given increasing interest in MOFs for storage and purification applications, workshop participants noted a need for standard synthesis methods to accelerate the pace of research. There are

many ways to synthesize these materials, and synthesis can be extremely challenging. Standard humidity testing methods and calculation methods for determining specific surface area would also be useful for MOFs. A standard naming scheme for MOFs would help to improve understanding of information in the literature. Additionally, a MOF reference material (sample and protocol) would enable inter-laboratory comparison studies.

Shale and Geologic Material Needs: The key research need for geologic materials is to improve available characterization methods at representative shale temperatures and pressures. The availability of a shale standard material would also be useful.

Mixture Adsorption and Surface Science Needs: Better understanding of mixture adsorption and selectivity was identified as the most critical research need for advanced materials development. There is a particular need for standard protocols and devices for mixture adsorption measurements, and to develop models that provide simulation results that are consistent with experimental results for adsorption of mixtures and polar molecules. Understanding chemoselectivity and the impact of surface chemistry on competitive adsorption is also an important challenge. Additional surface science challenges include understanding adsorption in dual-surface systems, understanding the complex effects of temperature and pressure on the behavior of probing molecules, and understanding the effects of intermediate compounds or by-product formation on adsorption.

Materials Design Needs: Modeling tools are needed to better understand the relationship between structure and properties and to accelerate adsorbent design. Novel structures are also needed to maximize adsorption/desorption kinetics.

Other Materials Research Needs: Adsorbent materials are typically available in the form of granules, pellets, powders, and beads. Structured adsorbents could provide numerous advantages, such as increased mass and heat transfer. Novel techniques are needed for measurements at very small scales, including both small pores (micropore and smaller) and small samples (thin films and small sample volumes). Novel contactors for integrated heat transfer could improve heat exchange for applications such as carbon capture. Finally, cost is a major limitation in the commercial use of adsorbent materials, and low-cost adsorbents are needed.

Table 3-2. Research Needs for Advanced Materials for Adsorption Applications
(● = one vote)

Metal–Organic Framework (MOF) Needs	
First Tier Priority	• Establish a standard naming scheme for MOFs ●●●
Second Tier Priority	• Develop a method to determine MOF adsorbate structure *in situ* ●
Third Tier Priority	• Develop standard synthesis methods for MOFs • Develop a standard simple humidity testing method for MOFs • Develop a standard method to calculate specific surface area (SSA) for MOFs • Make a standard MOF material available (reference sample and protocol)
Shale and Geologic Material Needs	
Second Tier Priority	• Improve shale characterization techniques, including methods for measurements at representative shale temperatures and pressures ●
Third Tier Priority	• Make a shale standard available (reference sample and protocol)
Mixture Adsorption and Surface Science Needs	
First Tier Priority	• Develop protocols and devices for mixture adsorption measurements and selectivity ●●●●●●●● • Reconcile experimental and simulation results for polar molecules and mixtures, especially water ●●●●●●●

Table 3-2. Research Needs for Advanced Materials for Adsorption Applications (● = one vote)	
	• Improve understanding of chemoselectivity (how does surface chemistry influence competitive absorption?) ●●●
Second Tier Priority	• Improve understanding of adsorption in dual-surface systems ●
Third Tier Priority	• Improve understanding of competitive adsorption, particularly in different phases (e.g., water vapor, carbon, hexane, mixtures) • Improve understanding of the complex effects of molecules used to probe sites at different temperatures and pressures • Improve understanding of intermediate compounds or by-product formation at the surface of the material
Materials Design Needs	
Second Tier Priority	• Develop structures and forms that maximize kinetics of adsorption and desorption ●
Third Tier Priority	• Design novel adsorbent materials using modeling, e.g., by understanding the structure–property relationships
Other Materials Research Needs	
First Tier Priority	• Transition from pellets, beads, and powders to defined structured adsorbents ●●
Third Tier Priority	• Make low-cost adsorbents available • Develop novel contactors for integrated heat transfer (e.g., using 3-D printing techniques) • Develop measurement devices that operate at the micron scale and smaller and provide accurate measurements for thin films and other small-scale samples • Develop methods for defining materials and making measurements at the micropore scale

POTENTIAL SOLUTIONS AND APPROACHES

Solutions were identified to address several of the most critical materials challenges:

Mixture Adsorption Measurements and Selectivity: Standard methods and procedures for adsorption measurements of gas mixtures would help to promote uniformity and better understanding across the field of how to make these challenging measurements. Simulation has strong potential as a complement to experimental studies, but good data are needed to help with model development. Therefore, adsorption should be measured on well-characterized material/gas combinations. The initial focus should be on the most important binary mixtures and industrially relevant conditions.

Standard Naming Schemes for MOFs: Development of new MOFs is stunted by a lack of naming conventions for new materials. Today, the same MOF may have more than one associated name. A structural topography-based naming convention would address these issues, but only with consensus in the community regarding the convention. A MOF definitions IUPAC recommendation would provide the needed reach within the community.

New Materials Development: New materials development could be accelerated through the use of advanced screening tools and computational design. One high-throughput screening strategy is to leverage molecular simulation tools to identify high-performance adsorbents from structural databases; this could reduce the time involved in synthesis and testing. Further, it would be useful to simultaneously optimize materials and processes at industrially relevant conditions.

Close Gap between Expertise, Materials, and Equipment: Pragmatic matchmaking is the key to closing gaps between availability of expertise, materials, and advanced measurement equipment. A website allowing users to

input facility capabilities and data could help to facilitate. Field practitioners should also find a way to communicate key instrument needs for research to equipment suppliers.

Further details of the suggested approaches are provided in Table 3-3.

Table 3-3. Potential Solutions and Approaches to Address Needs

Mixture Adsorption Measurements and Selectivity

• Define standard methods and procedures for mixture measurements
• Measure adsorption on well-characterized material/gas combinations to help develop potential for simulation
• Focus on the most "important" binary mixtures and conditions
• Adopt an industrial, not a fundamentals, approach (start with complexity and work down)
• Metrics:
  – Commercial equipment available with protocols for their use
  – Reference materials available with protocols for their use
  – Reproducible measurements

Standard Naming Scheme for MOFs
• Develop a structural topographic convention that will be acceptable given the challenges (today, the same MOF may have more than one associated name) • Establish consensus in community on naming convention—e.g., a MOF definitions IUPAC recommendation • Set meetings and identify proper community to make recommendations
New Materials Development
• Simultaneously optimize materials and processes, e.g., equilibrium isotherms for industrially relevant gases (methane, carbon dioxide, nitrogen) at industrially relevant hot conditions • Leverage molecular simulations to screen for high-performance adsorbents from structure databases
Close Gap between Expertise, Materials, and Equipment
• Provide assistance in matching expertise to materials (those with expertise do not always have access to materials; those with equipment do not always have access to materials) • Facilitate sharing of information, such as "how-to" guidance on building equipment • Develop a matchmaking website so that facility expertise and data can be entered

CHAPTER 4: DATA HARMONIZATION

EMERGING COLLABORATION TOOLS AND NEW TRENDS

Recent advances in the adsorption sciences have enabled scientists to make increasingly complex measurements, including kinetic studies, probing of microporous structures, and selective adsorption measurements. In many cases, sophisticated post-measurement analysis techniques are needed to make useful calculations from the measured data. At the same time, independent researchers are also sharing more data with the scientific community than ever before. Data are often posted as supplemental information with a published journal article, and the new NIST/ARPA-E database makes it simple for users to identify and download relevant data from other groups. Increasingly complex datasets combined with new collaboration tools have surfaced important issues related to data harmonization. For data to be comparable, researchers in the community must agree on how measurements and calculations are to be made and how data should be reported. Further, reference materials, standards, and data are needed to enable facilities to qualify their measurement equipment and ensure reproducibility of results.

RESEARCH NEEDS AND CHALLENGES

Data harmonization was a major theme throughout the workshop; participants identified needs for more consistent data reporting, greater availability of reference materials and standard protocols, and increased community engagement. Table 4-2 summarizes the key needs identified.

Data and Data Reporting Needs: Data are not reported consistently in the literature, and journal articles are often unclear on calculations and post-processing assumptions—resulting in data that cannot be compared across studies. As a result, accepted guidelines on measurements, data reporting, and data quality are needed. This should include a standard file format for data submitted as supplementary information with journal articles, and consistent software within commercial apparatus. An online data repository with a standard form of data could help to facilitate researchers' transition to a uniform data reporting standard. The NIST/ARPA-E adsorptive materials database provides an excellent start but would be even more useful if usability features were improved.

Reference Materials and Standards Needs: Reference materials and data for validation are needed for multiple classes of materials to enable data comparison and validation of test equipment. The protocol for choosing new reference materials should be clear. To ensure consistency, reference materials must be prepared with identical pre-treatment and activation conditions, and a protocol should be provided for monitoring stability. Useful information about the reference materials, such as sodium ratio and error bands, should be provided with the materials.

Community Engagement Needs: Connections between research scientists, equipment manufacturers, and others need to be encouraged to ensure that available equipment meets the needs of researchers and that work is not being duplicated or unnecessarily stalled. The adsorption sciences community would also benefit from conversations with those involved with the Cambridge Crystallographic Data Centre so that the community could benefit from what they have learned. NIST could take a principal role in educating field practitioners and educators on developments in the field.

Table 4-2. Research Needs for Data Harmonization and Standards (● = one vote)	
Data and Data Reporting Needs	
First Tier Priority	• Improve usability of NIST/ARPA-E adsorptive materials database ●●●●●●● • Encourage consistent, clear reporting of what is being measured/calculated (absolute vs. excess adsorption) ●●●● • Report data in a conventional manner ●● • Harmonize models and software within commercial apparatus ●●
Second Tier Priority	• Control data quality and reproducibility, especially for challenging measurements ●
Third Tier Priority	• Provide measurement and reporting guidelines • Establish a data repository with a standard form of data • Encourage use of a standard file format for submission of data as supplementary information to journal articles
Reference Materials & Standards Needs	
First Tier Priority	• Provide certified reference materials and data for validation for several material classes ●●●●●●●●●●●●● • Set uniform activation/pre-treatment conditions ●●●
Second Tier Priority	• Provide standards for high pressure isotherm measurements ●
Third Tier Priority	• Establish protocol for choosing new reference materials • Establish protocol for monitoring stability of reference materials • Standardize sample preparation for new materials (meta-standard) • For standard reference materials, include useful information with "certified" results, e.g., sodium ratio, error bands
Community Engagement Needs	
Third Tier Priority	• Promote better connections between materials scientists and equipment makers • Initiate connections/conversations with those "in charge" of the Cambridge crystallographic database so we can benefit from what they have learned • Engage community more fully (NIST could be at forefront to involve educators, practitioners on evolutions in the field)

POTENTIAL SOLUTIONS AND APPROACHES

Reference material availability and consistent data reporting were identified as the most critical challenges for data harmonization. Solutions were identified to address these needs:

Consistent Data Reporting: To promote consistent data reporting, it will be necessary to reach agreement within the adsorption sciences community on standard best practices for measurement, analysis, and data reporting. Reference material information could include documentation illustrating the relationships between different data workups, for example. Widely distributed example data sets that conform to IUPAC recommendations would benefit the community. Simple, open-source software for data manipulation and conversion (with example input and output) could also improve data uniformity. In the literature, it is important for authors to report enough information so that readers can understand the data; this could mean always publishing the original measurements to avoid confusion caused by miscommunication of assumptions and calculation procedures.

Reference Materials: Reference materials are needed for several materials categories, including zeolites, non-zeolites, materials with tortuous or ink bottle porosity, shales, and MOFs. Selection criteria for reference materials should include cost, repeatability, and lifetime, and pre-treatment protocols should be reported. To identify an appropriate MOF reference material, an expert panel could be assembled to identify a MOF that is representative in terms of activation, solvent removal, and synthesis technique. Reference data should be documented for a wide range of pressures, including high pressure measurements.

Round Robin Data Comparison: A multi-laboratory comparison (round robin) study should be performed using reference materials to validate measurement equipment and compare data across facilities. To ensure significance of results, this study should be statistically designed and carefully planned, specifying the number of laboratories, the measurements needed, and specific methodologies to follow. Participants recommended that testing be built around two or three high-impact materials and processes after identifying a range of relevant test cases. The NIST zeolite reference material would be a good starting place. Following the test, any discrepancies in the data should be thoroughly investigated.

Further details of the proposed solutions are provided in Table 4-3.

Table 4-3. Potential Solutions and Approaches to Address Needs

Consistent Data Reporting

• Reach consensus in the adsorption community on standard best practices for measurement, analysis, and data reporting
  – Provide simple open-source software for data manipulation and conversion, with example input and output
  – In reference material information, illustrate relationship between different data workups
  – Provide example data sets conforming to IUPAC recommendations
  – Ensure recommended practices are easy to implement
  – Work with equipment suppliers to establish standard data formats and reports
  – Ensure enough information is reported that data can be properly understood
• Metric: consistent data reporting in literature publications (number of papers)

Reference Materials

• Make reference materials available:
  – Zeolite material
  – Non-zeolite material
  – Material with tortuous or ink bottle porosity
  – Shale material
  – MOF material
• Provide selection criteria for reference materials, including repeatability, lifetime, and cost
• Form a MOF expert panel to identify MOFs that are representative in terms of activation, solvent removal, and synthesis technique; leverage the Cambridge database if possible
• Distribute pre-treatment conditions for reference material
• Report reference data in high pressure range, e.g., carbon dioxide adsorption on reference material
• Metrics:
  – Reference material available to community within one year
  – Reference materials and protocols appear in journals

Round Robin Data Comparison
• Design round robin study using statistical method to ensure significance of results • Identify a range of relevant test cases (e.g., 2–3 high-impact materials and processes) and build tests around them • Perform the round robin on one of the NIST zeolite reference materials; investigate any discrepancies

APPENDIX A: PARTICIPANTS

Alan Allgeier
DuPont

Ravi Kumar Arvapally
Virginia Commonwealth University

Brad Boyerinas
National Institute of Standards and Technology

Stefano Brandani
University of Edinburgh

Darren Broom
Hiden Isochema Ltd

John Bullis
QuantaPhi Corporation

Jinhong Chen
Aramco Services Company

Yudong Chen
Air Liquide Research

David Corbin
DuPont

Frieder Dreisbach
Rubotherm GmbH

Jeffrey Elks
BP Products North America

Laura Espinal
National Institute of Standards and Technology

Paul Forster
University of Nevada – Las Vegas

Sharon George
Springer Science

T. Grant Glover
University of South Alabama

Carlos Gonzalez
National Institute of Standards and Technology

Bob Grasso
W. L. Gore and Associates

Martin Green
National Institute of Standards and Technology

Katherine Hurst
National Renewable Energy Laboratory

Daniela Kohen
Carleton College

Shankhamala Kundu
W. R. Grace

Eric Lin
National Institute of Standards and Technology

Lifun Lin
Bose

Dongxia Liu
University of Maryland

Laurie Locascio
National Institute of Standards and Technology

Amanda McDermott
National Institute of Standards and Technology

Peter Monson
University of Massachusetts – Amherst

Bin Mu
Arizona State University

Alexander Neimark
Rutgers University

Dariusz Orlicki
W. R. Grace

Philip Parilla
National Renewable Energy Laboratory

Trong Pham
University of Delaware

Andrew Pomerantz
Schlumberger

Dianne Poster
National Institute of Standards and Technology

James Ritter
University of South Carolina

Meha Rungta
ExxonMobil

Eric Rohlfing
ARPA-E

Vincent Shen
National Institute of Standards and Technology

Daniel Siderius
National Institute of Standards and Technology

John Small
National Institute of Standards and Technology

Randall Snurr
Northwestern University

Orhan Talu
Cleveland State University

Matthias Thommes
Quantachrome Instruments

Michael Tsapatsis
University of Minnesota

Keita Tsuji
Microtrac

Roger van Zee
National Institute of Standards and Technology

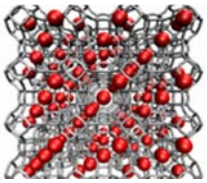
Artem Vityuk
BASF

Krista Walton
Georgia Institute of Technology

Keith Watson
Dow Chemical

Jennifer Wilcox
Stanford University

APPENDIX B: AGENDA



Workshop on Measurement Needs in the Adsorption Sciences

November 5-6, 2014 | NIST Advanced Material Laboratory, Building 215

Wednesday, November 5, 2014

08:00	**Bus departs parking lot of Hilton Washington DC North/Gaithersburg Hotel for NIST Campus**
	Introductory Session
08:45	**Roger van Zee** (Material Measurement Laboratory, NIST)
08:50	**Laurie Locascio** (Director, Material Measurement Laboratory, NIST)
08:55	**Eric Rohlfing** (Deputy Director for Technology, Advanced Research Projects Agency–Energy)
09:00	**Eric Lin** (Material Measurement Laboratory, NIST; Board Chair, Council for Chemical Research)
09:05	**Laura Espinal** (Material Measurement Laboratory, NIST) ***"FACT Capabilities"***
09:45	**Daniel Siderius** (Material Measurement Laboratory, NIST) ***"NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials"***
10:00	**Break**
10:15	**Tour:** NIST Facility for Adsorbent Characterization and Testing (FACT)
	Focus: Characterization Justin Gao (Corning)
11:15	**Alex Neimark** (Rutgers University) ***"Quenched Solid Density Function Theory of Adsorption for Heterogeneous Solids and Pore Structure Characterization"***
11:40	**Peter Monson** (University of Massachusetts, Amherst) ***"Understanding Adsorption/Desorption Hysteresis for Fluids in Mesoporous Materials using Simple Molecular Models and Classical Density Functional Theory"***
12:05	**Matthias Thommes** (QuantaChrome; Principal Scientific Advisor, FACT) ***"New IUPAC Recommendations: Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution"***
12:30	**Lunch**
	Focus: Advanced Materials for Adsorption Applications Jeff Elks (BP)
13:15	**Randy Snurr** (Northwestern University) ***"The Interplay Between Experiment and Simulation for the Design of New Metal-Organic Frameworks"***
13:40	**Krista Walton** (Georgia Institute of Technology) ***"Understanding the Stability of Metal-Organic Frameworks under Humid Conditions"***
14:05	**Jennifer Wilcox** (Stanford University) ***"***Characterization of Gas Shales for Enhanced Natural Gas Recovery and Carbon Storage Applications***"***

14:30	**Breakouts:** Facilitated small-group discussions of measurement science needs in adsorption sciences
16:15	**Break-out Summary Reports and Discussion**
16:45	**Return to hotel** (Bus)
18:30	**Reception at Hilton Washington DC North/Gaithersburg Hotel (Darnestown Room)**

Thursday, November 6, 2014

08:00	**Depart Hotel for NIST Campus** (Bus in hotel parking lot)
	Focus: Separations and Storage Applications Meha Rungta (ExxonMobil)
08:45	**Michael Tsapatsis** (University of Minnesota) ***"Two-Dimensional Zeolites for Separation Applications"***
09:10	**Jim Ritter** (University of South Carolina) ***"Frequency Response: A Powerful Technique for Discerning Gas Phase Diffusional Mechanisms and Rates in Nanoporous Adsorbents"***
09:35	**Orhan Talu** (Cleveland State University) ***"Role of Thermodynamics in Adsorptive Gas Storage Applications"***
10:00	**Breakouts:** Facilitated small-group discussions of measurement science needs in adsorption sciences
	Workshop Wrap-up
11:30	**Summary and Next Steps**
12:15	**Adjourn** (Box Lunch Available)
12:30	**Bus to Hotel**

Breakout Session Chairs:

- **Characterization:** Alan Allgeier, DuPont
- **Advanced Materials for Adsorption Applications:** Jinhong Chen, Aramco Services Company
- **Separations and Storage Applications**: Stefano Brandani, University of Edinburgh

APPENDIX C: ACRONYMS/ABBREVIATIONS

BDC	1,4-benzenedicarboxylate
BET	Brunauer-Emmett-Teller (theory of adsorption)
CCR	Council for Chemical Research
CRADA	Cooperative Research and Development Agreement
DFT	Density Functional Theory
DMOF	1,4-diazabicyclo[2.2.2]octane (DABCO) Metal-Organic Framework
FACT	Facility for Adsorbent Characterization and Testing (NIST)
FTIR	Fourier Transform Infrared Spectroscopy
IP	Intellectual Property
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
MFI	Mordenite Framework Inverted (zeolite)
MIR	Multiple Internal Reflection (spectroscopy)
MOF	Metal–Organic Framework
MML	Material Measurement Laboratory (NIST)
MWW	Mobil Crystalline Material No. 22 (MCM-tWenty-tWo)
NiChE	New Industry and Chemical Engineering (workshop)
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance (spectroscopy)
NSDFT	Non-Local Solid Density Functional Theory
PSA	Pressure Swing Adsorption
QSDFT	Quenched Solid Density Functional Theory
RH	Relative Humidity (%)
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction