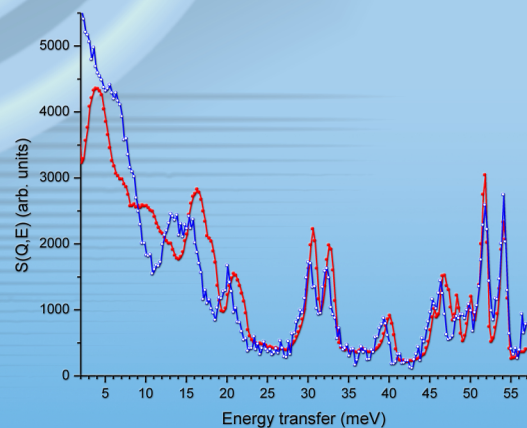
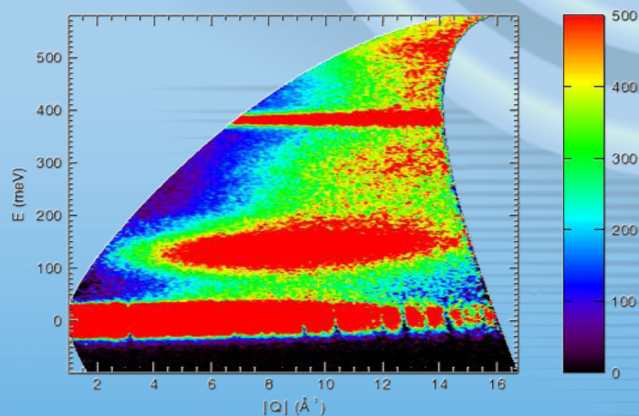
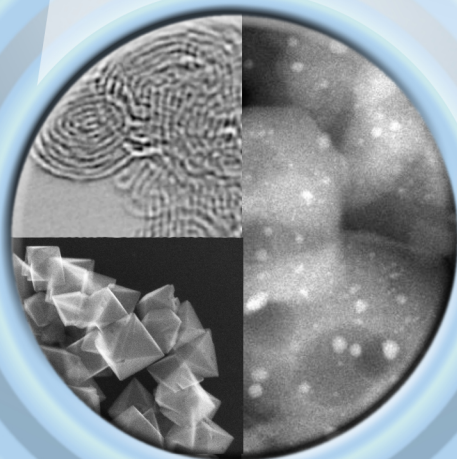


# Neutrons for Catalysis: A Workshop on Neutron Scattering Techniques for Studies in Catalysis

Oak Ridge National Laboratory  
Spallation Neutron Source  
September 16–17, 2010



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Oak Ridge National Laboratory

Spallation Neutron Source

September 16–17, 2010

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**Meeting sponsored by**

**ORNL Neutron Sciences and Physical Sciences Directorates**

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**Oak Ridge Associated Universities**

**Fluid Interface Reactions, Structures and Transport (FIRST),  
an Energy Frontier Research Center**





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## **Executive Summary**

This report summarizes the Workshop on Neutron Scattering Techniques for Studies in Catalysis, held at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) on September 16 and 17, 2010. The goal of the Workshop was to bring experts in heterogeneous catalysis and biocatalysis together with neutron scattering experimenters to identify ways to attack new problems, especially Grand Challenge problems in catalysis, using neutron scattering. The Workshop locale was motivated by the neutron capabilities at ORNL, including the High Flux Isotope Reactor (HFIR) and the new and developing instrumentation at the SNS. Approximately 90 researchers met for 1 ½ days with oral presentations and breakout sessions. Oral presentations were divided into five topical sessions aimed at a discussion of Grand Challenge problems in catalysis, dynamics studies, structure characterization, biocatalysis, and computational methods. Eleven internationally known invited experts spoke in these sessions. The Workshop was intended both to educate catalyst experts about the methods and possibilities of neutron methods and to educate the neutron community about the methods and scientific challenges in catalysis. Above all, it was intended to inspire new research ideas among the attendees. All attendees were asked to participate in one or more of three breakout sessions to share ideas and propose new experiments that could be performed using the ORNL neutron facilities. The Workshop was expected to lead to proposals for beam time at either the HFIR or the SNS; therefore, it was expected that each breakout session would identify a few experiments or proof-of-principle experiments and a leader who would pursue a proposal after the Workshop. Also, a refereed review article will be submitted to a prominent journal to present research and ideas illustrating the benefits and possibilities of neutron methods for catalysis research.

## Introduction and Goals

The Department of Energy (DOE) report *Basic Research Needs: Catalysis for Energy*,<sup>1</sup> a report of a DOE Office of Basic Energy Sciences Workshop held in August 2007, identified catalysis as “the essential technology for accelerating and directing chemical transformation” and “key to realizing environmentally friendly, economical processes for the conversion fossil energy feedstocks.” The document summarized the research needs and opportunities for catalysis to meet the nation’s energy needs, provided an assessment of where the science and technology now stand, and recommended directions for fundamental research that should be pursued to meet the goals described. Catalytic technologies account for over \$1 trillion in revenues in the US economy and about one-third of its material GDP, according to the 2009 World Technology Evaluation Center report *An International Assessment of Research and Development in Catalysis by Nanostructured Materials* (<http://www.wtec.org/catalysis/>), funded by the National Science Foundation, DOE, Air Force Office of Scientific Research, and the Defense Threat Reduction Agency. According to the report, “Catalysts are considered the engines that power the world at the nanometer scale and are generally considered to be the most successful application of nanotechnology.”

Improving understanding of general catalysis science and technology is important, and the next step needs to be to focus on the value added by using neutron scattering. Oak Ridge National Laboratory (ORNL) is the home of the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR), two of the world’s premier centers for the study of matter using neutron analysis and neutron scattering techniques. ORNL has been involved in a number of outreach events to scientific communities—such as the Workshop on Imaging and Neutrons (2006) and the Dynamics of Soft Matter Workshop (2008)—that have helped neutron scattering scientists understand these communities’ research needs. Workshops of this type were identified in the report *Building A Network for Neutron Scattering Education* by Roger Pynn et al. (ORNL/TM-2008/201, <http://info.ornl.gov/sites/publications/files/Pub13283.pdf>). It called for the neutron scattering community to lower the barriers that prevent scientists from using neutron scattering, encourage scientists from fields that do not traditionally use neutron scattering to try the technique, and expand the pool of scientists who appreciate the contributions that neutron scattering make to solving important scientific problems.

The workshop goals of the Neutrons and Catalysis Workshop were identified as the following:

- Bring leaders in the catalysis community together with experts in neutron scattering to explore how Grand Challenge problems in catalysis can be explored using neutron methods.
- Educate potential users in the catalysis community about the opportunities, limitations, and availability of neutron methods for performing their experiments.
- Educate neutron scattering researchers and instrument scientists about the needs and interests of the catalysis community.

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<sup>1</sup> The report is available at [http://science.energy.gov/~media/bes/pdf/reports/files/cat\\_rpt.pdf](http://science.energy.gov/~media/bes/pdf/reports/files/cat_rpt.pdf).

Help users identify their own proof-of-principle experiments.

- Position ORNL user facilities to enable world-class catalysis research.

The success of the workshop depended on enabling experts in catalysis to describe their challenges and interact with neutron scattering experts. It provided a setting for the national neutron user community within this diverse group to strengthen ties among themselves while also promoting neutron research among colleagues in related disciplines identified as potential neutron users. As a venue for scientific exchange, the workshop showcased recent results and provided forums for scientific discussion through a combination of invited talks and breakout sessions. Key to this approach was identifying neutron scattering experiments that could form the basis of future research directions. The following topical areas were emphasized:

- Identification of Grand Challenges that could be attacked using neutron methods
- Probing dynamics of molecules in catalyst systems by inelastic neutron scattering
- Modeling of catalysts, catalysis, and neutron experiments
- Structural characterization of catalysts and catalytic materials
- Probing biocatalysis by neutron scattering methods

The planned output of this action-oriented workshop is

- Identification of proof-of-principle catalysis experiments using neutrons that would be awarded beam time in 2011
- A report describing the workshop
- A session at a future American Chemical Society annual meeting
- A published article that contains a critical review of the current state of the use of neutron scattering methods for the study of catalysis and presents essential aspects of the discussions deriving from the workshop

More broadly, perhaps the most important outcome of this approach is that the ORNL neutron scattering user facilities will expand their potential user base, diversifying both scientific disciplines and the pool of individual researchers. The workshop and its output will encourage future participation from colleagues in the catalysis community who will achieve an improved understanding of the range of possible neutron scattering experiments, putting them in an improved position when submitting proposals for future beam time.

## **2. Summary of Topical Sessions**

Michelle Buchanan, Associate Laboratory Director for Physical Sciences at ORNL, opened the workshop. Her message was that SNS is opening up new capabilities for science that researchers in the Chemical and Material Sciences have not yet fully exploited, and that there are exciting possibilities for exploring new science and, for example, performing in situ catalysis experiments with neutrons. The purpose of the workshop is to get member of the catalysis



community together with those in the neutron scattering community to help ORNL raise awareness about how the SNS and HFIR can support the catalysis community. Buchanan emphasized the importance of “socializing” the results of the workshop and of all participants contributing, with the goal being to find common ground and explore research opportunities. The output of the workshop will be (1) user proposals to SNS and HFIR from the catalysis community and (2) a written report available to the community that will describe the opportunities and show the catalysis community how neutron methods can be used in their science.

A DOE perspective was provided by Pappannan “Thiyaga” Thiyagarajan, program manager for Neutron Scattering in DOE’s Materials Sciences and Engineering Division of Basic Energy Sciences. This program is responsible for planning and operation of the neutron facilities. Thiyagarajan presented the BES organization chart related to neutron and catalysis science showing the broad commitment of BES to both catalysis and to the development and use of neutron scattering. He presented the catalysis goals described by the DOE Chemical Sciences, Geosciences, and Biosciences Division as being

- to understand the origin and evolution of catalytic properties across scales of space and time
- to develop the predictive science of catalytic reaction mechanisms and structures
- to use inspiration from nature for manipulating and creating new catalyst structure and dynamics

Thiyagarajan provided a snapshot of the broad spectrum of research in catalysis sciences that showed a multifaceted and diverse program with about 140 projects that can be divided into 24 topical areas including bond activation, ultra-fast processes, chemical imaging, oxidation catalysis, inorganic synthesis and single site catalysts, enzyme chemistry, photocatalysis, hydrogen storage and biomass conversion. He described the neutron scattering program at DOE’s Materials Science and Engineering Division as basic research on the fundamental interactions of neutrons with matter, aimed at achieving an understanding of atomic, electronic, and magnetic structures and excitations of materials. The program is evolving at the interface between hard and soft materials and focuses on energy related materials. Initially there was an emphasis on instrument development but now it is moving more to science-driven goals. Thiyagarajan provided a list of the properties that make neutron scattering a unique tool for structure and dynamics (Table 1).

He emphasized the ability to see low-mass, “difficult” atoms in the presence of more massive atoms, for example, the ability to study hydrogen in metallorganic frameworks. He described three major types of funding programs from DOE: core research (single investigator and small groups, Energy Frontier Research Centers (multiple investigators), and Energy Innovation Hubs (large \$20M+ research centers), that he expected would benefit from neutron scattering capabilities. These programs and workshop reports that contributed to them are described at the BES Web site (<http://science.energy.gov/bes>). Thiyagarajan noted the Neutrons and Catalysis Workshop is timely because new neutron scattering instruments are just coming on

line, and many of the new Energy Frontier Research Centers contain catalysis in their core research portfolios.

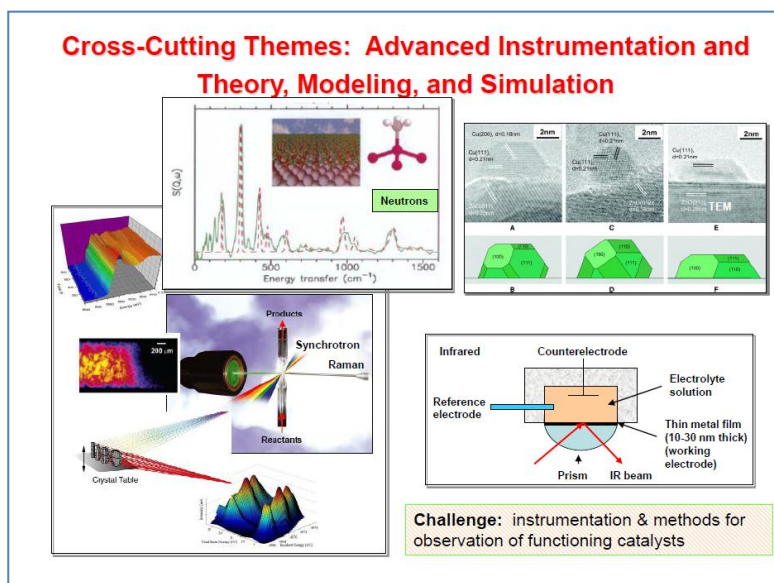
<b>Table 1. Neutron scattering—unique tools for structure and dynamics</b>
Unique scattering cross-sections to enable visualization of light and heavy atoms in complex materials, e.g., zeolites, metallorganic frameworks
Larger differences in scattering cross-sections of certain isotopes, enabling unique contrast variation studies of multicomponent systems, e.g. hydrogen and deuterium
High penetration of neutrons, enabling easy access to complex sample environments
In situ capabilities at the highly optimized instruments at the SNA and HFIR with the highest pulsed and steady state neutron flux
Accurate determination of protonation states and hydrogen bonding networks
Dynamics of systems in the ps to ms time scales through a range of inelastic, quasielastic and spin-echo neutron scattering techniques

Following the introductory remarks by Buchanan and Thiyagarajan, formal presentations from the invited speakers began. The sections below briefly describe the goals and motivations of each of the sessions, as conceived prior to the workshop, and summarize the presentations of each of the invited speakers. The presentations can be found at the workshop Web site at <http://neutrons.ornl.gov/conf/NandC2010/talks.shtml>.

## 2.1 Meeting Grand Challenges in Catalysis through Neutron Scattering

The goal of this session was to discuss Grand Challenge problems in catalysis and explore how neutron scattering could contribute to solving them. Experts in catalysis were to identify Grand Challenge problems and current research approaches to solving them, with emphasis on areas where neutron-based techniques are expected to contribute. Experts in the use of neutron scattering were asked to provide a broad survey of past and current accomplishments in using neutron methods for studies of catalysis and catalytic materials. Bruce Gates of the University of California–Davis and Juergen Eckert from University of California–Santa Barbara were the presenters in the session, which was moderated by Ken Herwig and Phil Britt, both of ORNL.

Gates’s presentation was titled “Meeting grand challenges in catalysis through neutron scattering techniques.” Gates was a leader of the workshop that led to the report *Basic Research Needs: Catalysis for Energy* ([http://science.energy.gov/~media/bes/pdf/reports/files/cat\\_rpt.pdf](http://science.energy.gov/~media/bes/pdf/reports/files/cat_rpt.pdf)); neutron scattering is one of the crosscutting themes discussed in the report (Figure 1). Gates emphasized that



**Figure 1. Examples of cross-cutting and complementary techniques used for probing catalysts.**

temperatures and pressures and in contact with complex mixtures. One important approach is the use of well-defined catalysts as a tool to aid understanding of complex catalyst structures.

Gates discussed a few “snapshot” examples of incoherent inelastic neutron scattering (IINS) in catalyst characterization; hydrogen featured in several of them. He cited studies of zeolite-supported  $\text{Ir}_6$  clusters probed by  $^1\text{H}$  nuclear magnetic resonance (NMR) and neutron scattering that reveal both OH groups on the zeolite and  $\text{IrH}$  species, even in the absence of hydrogen in the gas phase. However, this example did not include measurements under reaction conditions. In other work, Eckert and Goodman pushed measurements of catalysts to post-mortem studies (i.e., after exposure to reaction conditions). A hydro-peroxy species was found following epoxidation conditions that may play a role in the conversion. It is clear that IINS data have a high information content. Gates returned to the theme of complementarity by showing a list of techniques that have been used to characterize catalysts under working conditions, including infrared (IR) spectroscopy in the top spot, but also x-ray scattering techniques such as extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge spectroscopy (XANES). The community is learning how to perform multiple techniques in tandem, realizing that different methods may complement one another. There are enormous possibilities for combining techniques, and researchers should ask themselves where neutron methods fall into this categorization. An area that should be addressed, Gates said, is how scientists can watch changes in a catalyst in real time under transient conditions while continuously monitoring reaction products. How can we optimize IINS in concert with complementary experimental techniques? Since neutron measurements permit new ways to study catalysts under high-pressure environments, then these can be an important complement to other in situ types of measurements.

The discussion following Gates’ talk touched on the importance of being able to probe pore structure and reactions in pores in working catalysts. The ability to monitor movements not

addressing energy needs will require understanding catalytic transformations in new feedstocks. Using new sources of fossil fuels and renewable biofuels implies challenging conversions and completely different catalytic systems. Hydrogen is a key element in all of these future feedstocks, so neutron scattering capabilities will be needed. The question of “how catalysts work while they are working” is critical; therefore, there has been a drive to combine a variety of techniques to understand catalysts under reaction conditions, often at high

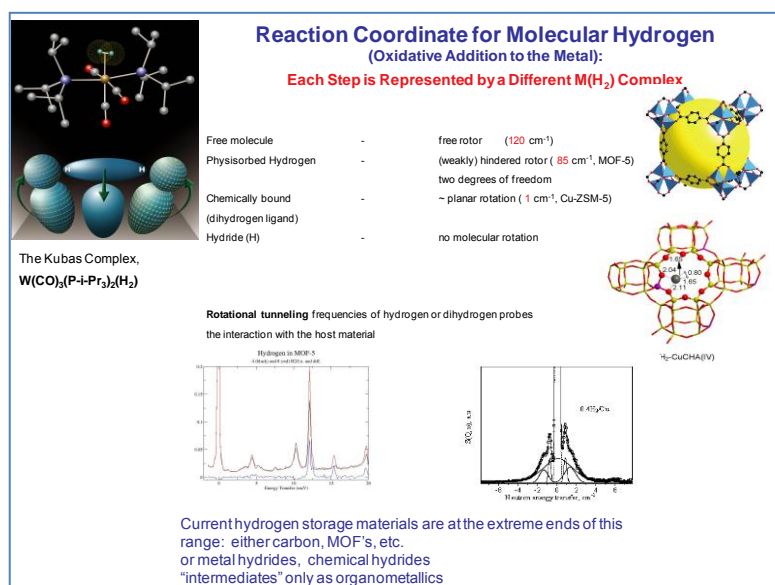
only of molecules across surfaces, but also of the composite atoms in catalytically active clusters, (e.g., writhing modes of hydrogen in iridium clusters) would be an important outcome of neutron studies. Gates mentioned the importance of the new in situ microscopy and the opportunity to explore using microscopy and neutron methods in tandem to observe changes in structure. In addition, it would be important to couple such experiments with computational methods to get predictive capabilities of catalyst structures in motion.

Eckert presented a talk titled “Neutrons as microscopic probes in heterogeneous catalysis.” He noted that a basic problem of doing in situ measurements is that the equipment is frequently not available. In past, it was often the catalyst user who supplied the necessary in situ equipment. For IINS experiments, working at low temperatures is preferred because it results in better spectra; but small-angle neutron scattering (SANS) and quasi-elastic neutron scattering (QENS) experiments can be performed at any temperature, and in situ experiments using those techniques should be “easy.” Eckert discussed two topics from the BES report that are relevant to neutrons: (1) reaction mechanisms and (2) the design and controlled synthesis of catalytic structures, including highly uniform catalysts, large-pore zeolites, and biomimetic catalysts. For reaction mechanisms, he noted the importance of accurate measurement of selected model systems as benchmarks for theory development and the use of multiple techniques to obtain information over wide time scales. Important properties of neutrons related to design and controlled synthesis is their ability to probe both structure and dynamics, their low absorption cross-sections for sample containers, isotope-dependent scattering, and ease of complementary computational studies.

Eckert presented examples of using neutrons to probe catalysts, including these:

- Studying the structure of the active site in micro- and mesoporous model titanium silicates, in which the highly different cross sections of titanium and silicon made it possible to explore the location of titanium in TS-1 or iron in silica zeolites by powder neutron diffraction. The researchers found five sites that contain the titanium.
- Studying the interaction of water with H-ZSM5 zeolites to find the sites on which the water adsorbs and calculate the result. Researchers discovered that H<sub>2</sub>O is the adsorbed site rather than H<sub>3</sub>O<sup>+</sup>. [H. Jobic et al., *J. Phys. Chem.* **100**, 19545, 1996]
- Exploring the binding of chloroform in NaY zeolites to discover from a combination of IINS and computational modeling that the observed C-H shift is the signature of an orientational shift of the molecule indicative of CH<sub>3</sub>O bonding to the zeolite. [C. F. Mellot, A. Davidson, J. Eckert and A. K. Cheetham, *J. Phys. Chem.* **102**, 2530, 1998] The location was established by differential neutron pair distribution function analysis (nPDF). [J. Eckert, C. Mellot-Draznieks and A. K. Cheetham, *J. Am. Chem. Soc.* **124**, 170, 2002]
- Probing the bonding of acetylene on NiNaY in zeolite enhanced using isotopic enrichment with <sup>62</sup>Ni. Nitrogen partial pair distribution function gave C-Ni bonding distances to determine acetylene bonding site. [J. F. C. Turner et al. *J. Phys. Chem B* **104**, 7570, 2000]
- Measuring the diffusion of benzene in faujasite using QNS to learn that benzene jumps from one cation site to another. [Jobic et al. *J. Phys. Chem. B* **104**, 8491, 2000]
- Studying hydrogen spillover from Ir<sub>6</sub> clusters onto sodium zeolite-Y support using IINS [F. Li, P. Yu, M. Hartl, L. L. Daemen, J. Eckert, and B. C. Gates, *Z. Phys. Chemie* **220**, 1553, 2006]

- Studying the reaction coordinate of H<sub>2</sub> molecule with metal sites by IINS to determine whether the H<sub>2</sub> molecule is coordinated to metal sites (see Figure 2). This is important for understanding H<sub>2</sub> storage.
- Using IINS to study propylene oxide formation on Au/TiO<sub>2</sub> is an example of how to quench a reaction for post-mortem IINS studies. The study found that the propylene oxide skeletal modes are strongly affected by adsorption, but extensive computational work is needed to sort out the spectral changes.
- Determining the catalytic decomposition of methane by similar quench techniques. It was concluded that computational studies are required for proper identification of Intermediates, products, and reaction mechanism. [C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert and D. W. Goodman, *Angew. Chem. Intl. Ed.* **41**, 144, 2002]
- Determining by IINS that the deactivation of a palladium catalyst is due to methyl groups that form on the catalyst under reaction conditions. [Albers et al., *Chem. Com.*, **1619**, 1999]



**Figure 2. Use of neutron methods for studies of hydrogen bonding in hydrogen storage materials.**

Touching on what he sees as future research directions, Eckert mentioned high-surface-area catalysts of nonprecious metals. He concludes that in situ research on these materials can be done at appropriate temperature and pressure if equipment can be made available. Computational models for model systems are very important and suggest that single-crystal studies are important. Only one single crystal experiment has been done on zeolites, because there are problems in growing large crystals in these systems. The SNS instrument TOPAZ is expected to lower the crystal size required for these types of studies. It will be important to probe structure–function relationships. We may get closer to understanding reaction mechanisms by studies of molecular diffusion dynamics in concert with computational studies.

Discussion following Eckert's talk provided several points of clarification. There were questions about the duration of experiments (it depends upon amount of hydrogen in the sample and the neutron flux), whether neutron experiments can determine total hydrogen content (yes, but it is challenging in IINS and slightly easier in diffraction), and whether hydrogen can be detected at high temperatures by IINS (it depends upon how strongly bound the hydrogen is). Eckert noted that although spectra he showed required 12 hours, the experiments would go much faster at the SNS. He also noted that diffraction is much faster and more suitable for real-time experiments.



## 2.2 Probing Dynamics of Molecules in Catalyst Systems by Inelastic Neutron Scattering

The focus of this session was how inelastic neutron scattering, both coherent and incoherent, can be used to probe various dynamics and processes involving molecules in catalyst systems. Because the neutron scattering cross section does not scale with the atomic number, it is often possible to probe the dynamics of adsorbent molecules (e.g., water or hydrocarbons) in much heavier matrices (e.g., metals, oxides, or porous media), which would be impossible with x-rays. In particular, the incoherent neutron scattering cross section of hydrogen is especially high compared with all other elements. This allows exploration of diffusion dynamics and transport properties of hydrogen-bearing species associated with both homogeneous and heterogeneous catalytic processes over wide ranges of time (sub-picoseconds to nanoseconds) and length (angstroms to nanometers) using QENS. The dynamics of such processes can be probed over even longer time scales (up to sub-microsecond) and length scales (tens of nanometers) using neutron spin echo (NSE). On the faster time scale, the dynamics of molecular vibrations can be probed by IINS. This technique is also sensitive to hydrogen-bearing species and can provide valuable information about the site environments and chemical bonding of the molecules. Because the incoherent scattering cross section of deuterium is much lower than that of hydrogen, selective deuteration can be used to isolate specific reactant and product species and even the dynamic properties of portions of more complex molecules. Inelastic neutron scattering is also capable of probing the dynamics of non-hydrogen-bearing species, such as, e.g., CO<sub>2</sub>; in such a case, QENS or NSE can be used to probe coherent scattering from the atoms in the mobile molecules (e.g., carbon or oxygen). The high-intensity neutron beam generated at SNS and the unique BASIS, CNCS, NSE, ARCS, SEQUOIA, and VISION spectrometers, combined with the high penetration power of neutrons, have made it possible to follow molecular dynamics and explore in situ catalytic reaction under *operando* conditions. Steve Overbury and Dave Wesolowski were the session moderators.

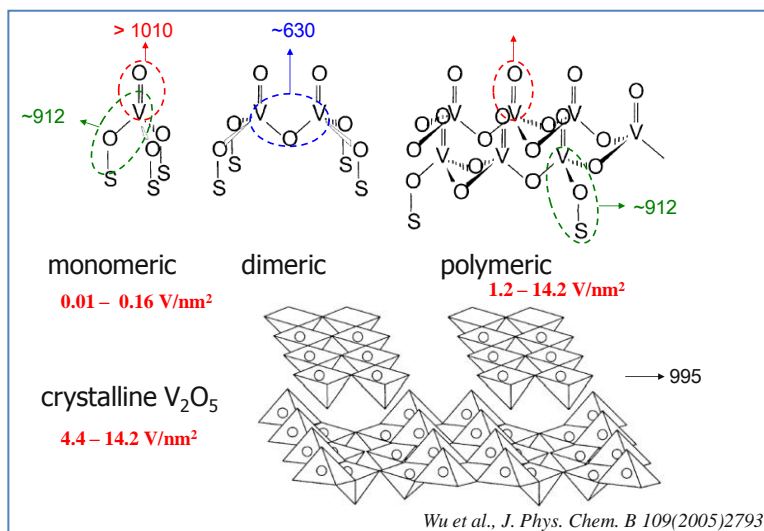
Peter Stair of Northwestern University provided perspective on the catalytic question of the presence and role of hydroxyls that are ubiquitous to many catalytic systems. (His talk was entitled “Some thoughts about surface hydroxyl groups and catalysis.”) The open question is whether neutron methods would be useful for studies in this area. Stair described his experiments on growing films, especially supported vanadia oxide catalysts, using atomic layer deposition processes (Figure 3).

Little is known about the structure of the vanadia species, how many types there are, how they are bonded to the surface and whether hydroxyls are linked to the vanadia species. The role of hydroxyls on the supports ( $\Theta$ -alumina and  $\Upsilon$  alumina) is also of interest. To date, most of what is known about the vanadia species has been obtained by Raman and resonance Raman experiments. Hydroxyl species associated with vanadia species can't be seen from the hydroxyl region in Raman, but their effects are seen in the vanadyl features and suggest that there is more than one type of monomeric VOx species. Reduction treatments show that these species transform at different temperatures, implying that the structure and possibly the hydroxyl groups are different. The species also depend upon which supports are used and the type of vanadia precursor that is used to prepare the films. So it appears that these species have

different hydroxyl species, but we don't know because we can't see them. Computational methods can provide additional insight but it would be helpful to have other experimental techniques that can see the hydroxyls directly.

Questions and comments following Stair's talk clarified the presentation and pointed to possible neutron experiments:

- A question from Bruce Gates regarding the origins of assignments brought out that measurements on reference compounds and theory are the basis for vibrational assignments. It was noted that density functional theory cannot give accurate frequencies, although the computed energetics and the relative ordering of vibrational frequencies can be very useful.
- Simon Bare commented that most catalysts are mixtures of sites, leading to the question whether there are "neutron tricks" for emphasizing particular components or trace species. Bare also commented that there are many systems in which water or trace amounts of hydroxyls are known to play an important role in catalytic activity and in sintering of catalysts.
- A. Kolesnikov said it is possible to address many questions by working at large energy transfers and low momentum transfers to look at the stretching OH modes. The intensity of the modes can be normalized to get the number of OH species. Also, since the stretching frequency depends upon the strength of the hydrogen bond, the use of reference molecules may provide answers to many of the questions raised in Stairs' presentation.
- Stair noted that probe molecules could be very useful, citing the example of CO as a probe molecule in surface experiments. Is there a probe molecule for hydroxyl species that could be used in neutron experiments?
- Since interpretation of IINS relies heavily on theory, is theoretical support available from SNS?
- Takeshi Egami pointed out that hydrogen and vanadium are unique species for neutrons. Vanadium is almost invisible, but combining hydrogen and deuterium can help to differentiate the vanadia species. A problem with this approach (for example, in selectively deuterating the vanadia) is that the hydrogen-deuterium exchange may be rapid so that the initially deuterated moieties will be scrambled.
- Use of crystalline nanoparticles supports may aid in making better defined samples, for example, making acid sites identical. It was also suggested it would make sense to use MgO as a more uniform support for vanadia instead of alumina. Similarly, by changing between



**Figure 3. Models of vanadia species that may be present on support surfaces.**

specific precursor molecules, it may be possible to select specific adsorption sites or structures.

- Dave Wesolowski asked if QENS or NSE techniques can be used to probe domain sizes of hydroxyl-containing species or the mobility of protons. Juergen Eckert pointed out that proton hopping from hydroxyl is too slow to be seen.
- What are the results of comparisons of IR and neutron measurements in agreement in cases where structures have well-defined and well-characterized hydroxyls (e.g., zeolites)? Eckert pointed out that this comparison has not been made because resolution in the stretching region is bad for kinematic reasons, and the bending region is not accessible by IR because it is dominated by silica modes. This comparison may now be possible using SEQUOIA at the SNS.
- There are combination modes due to hydroxyls in higher-frequency regions near 4500 to 5000  $\text{cm}^{-1}$  that can differentiate hydroxyls. These are combination bands and may be difficult to see by Raman, but IR shows them very nicely.

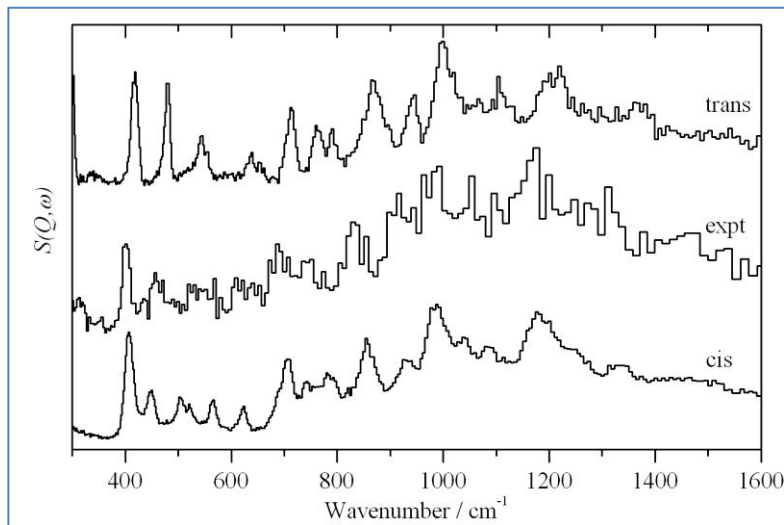
Peter Albers of AQura presented an industrial view of using neutron methods (“Practical applications in the chemical industry: proton dynamics of technical catalysts and materials from operating large scale plants, hydrogen on fuel cell catalysts”). He described a case in which a palladium catalyst in a processing plant became deactivated for unknown reasons. Efforts to find the problem by Raman, IR, NMR, sorption analysis microscopy, elution, and elemental analysis all failed. His team examined the catalyst using IINS and found evidence for methyl species; that finding explained the deactivation observed at the plant, which changed the adsorption properties of the palladium surface vs.  $\text{sp}^2$ -type molecules but not the uptake of hydrogen into the bulk of the palladium particles. A history of a deactivation process could be recorded by probing the dynamic changes of the carbon-related surface chemistry over several months. The problem of stable  $\text{CH}_3$ -entities is also relevant in hydrogenation of syngas, Fischer Tropsch catalysis, and conversion of biomass into diesel fuels. Reaction volumes are large in industrial catalysis, and the engineers appreciated the ability of neutron methods to look at representative volumes of catalyst.

In another example, Albers described the issue of coke formation in the vinyl chloride manufacturing process and a step for selective hydrogenation of acetylene to ethylene. In addition to carbon buildup expected from microscopy (polymer- or CVD- coke), neutron scattering showed evidence of an unexpected  $\text{Fe}(\text{H}_2\text{O})\text{Cl}_5$  chloride complex that was also playing a role in deactivation and coking. IINS offers high and unexploited potential in a deeper characterization of low- and high-temperature cokes from industrial plants, as well as diesel soot and other carbonaceous matter.

Another example was related to probing hydrogen terminations in carbon blacks, especially in fuel cells. The challenge is to identify and distinguish hydrogenic species from  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , Pt-H, C-H, PtRu-OH. Using IINS, it was possible to distinguish Pt-H features that vary with platinum particle size, indicative of differences in platinum adsorption sites [ (100) vs (111)]. Future work will consider proton dynamics and hydrogen site titration to look at disorder and defects in nanoparticles supported on high-surface-area supports.

Albers also discussed the heterogenization of homogeneous catalysts to control precious metal inventories for catalysts used in C-C coupling reactions. IINS spectra are able to differentiate between trans- and cis- isomers of stilbene (Figure 4), from which researchers learned that the cis-isomer is more strongly adsorbed to the carbon surface, a fact attributed to the stronger interaction with the carbon edges. Usually it is assumed that educts and products are adsorbed to a similar degree, but this is not the case in these two isomers. This preferential adsorption is also relevant for catalytic hydrogenation reactions. Albers stated that IINS is a helpful and versatile technique for the solution of problems in (e.g.) industrial R&D, materials research, applied catalysis, and various other areas, especially when all other analytical methods fail.

Discussion of Albers' presentation focused largely on access to and use of SNS for proprietary and industrial research. Albers was asked how he succeeded in convincing his company to use neutrons, what mechanisms are available for getting beam time at SNS, and what motivates researchers at ISIS (or SNS) to collaborate in industrial work. His answer was that there is a high activation barrier for getting management to agree, but pain in production problems and failure of all other approaches can be a compelling argument. Work comes about partly by writing proposals for beam time, but in some cases beam time was paid for directly. In many cases, his company performed experiments that were sufficiently fundamental that the results could be published—a motivating factor for more science-oriented collaborators. It was noted that both proprietary and fast access time is available at SNS and HFIR.



**Figure 4. IINS spectra for comparison of cis and trans- isomers of stilbene, and experimental spectrum of what is present at the catalyst surface after the organic phase is removed.**

The third speaker in the session was Eugene Mamontov, an instrument scientist for the Backscattering Spectrometer (BASIS) at SNS (Figure 5), whose topic was “What can we learn about the mobility of species in catalytic systems using quasielastic neutron scattering” (QENS). He discussed the time and energy used in neutron experiments to show that QENS like those performed on BASIS probe dynamics in the range of 10 ps to 1 ns. Since cold neutrons have energies in the meV range, it is possible to observe energy transfers in the range of 1  $\mu$ eV associated with jump diffusion processes, making them intrinsically suitable for probing these types of dynamics. BASIS can measure scattering at many different values of the momentum transfer, or Q, simultaneously; and both the relaxation times and diffusion process geometry are determined through the Q-dependence of the QENS broadening. From fitting such data to a



**Figure 5. Eugene Mamontov and Ken Herwig inside BASIS.**

jump diffusion model, it is possible to get information about translational diffusion in confined liquids, extracting diffusion coefficient, time between jumps, and jump lengths. Mamontov also explained how it is possible to get information about the confinement geometry in porous materials and about rotational (nontranslational) diffusion; for example, reorientation of benzene in

crystalline state or rotations of molecules adsorbed in zeolites. Systems that can be studied are usually hydrogenous because of the large hydrogen incoherent cross section. It is possible to study motions associated with other types of atoms but only if either there is no hydrogen in the system or if all of the hydrogen is replaced by deuterium. This was illustrated by studies of  $\text{CO}_2$  diffusion in the presence of  $\text{CH}_4$ . Another issue is studies of oriented samples such as single crystals or wafers. The problem is that there must be at least a mmol of hydrogen in the sample to observe. So a recent approach was to use multiple (up to a hundred per sample) wafers to get enough signal. In principle it would be possible to study a monolayer on multiple oriented wafers, but this would require long measurements of samples consisting of thousands of very thin wafers. Next Mamontov went on to discuss studies of water adsorption and dynamics of motion at oxide surfaces. He discussed experiments on  $\text{TiO}_2$  and  $\text{SnO}_2$  surfaces. QENS results were compared with x-ray scattering results that identify three distinct structural regions (layer 1, 2 and 3; L1, L2 and L3) corresponding to three layers above a  $\text{TiO}_2$  surface [Mamontov, Wesolowski, Vlcek, Cummings, Rosenqvist, Wang, Cole, *Journal of Physical Chemistry C* **112**, 12334 2008]. Each of these layers has different water molecule dynamics.

- Slow dynamics (100s ps–1 ns): L2-L3 exchange jumps (analogous to translational jumps in bulk water)
- Intermediate dynamics (10s–100s ps): Localized (rotation-like) motion mostly in L2 and L3 (analogous to rotational jumps in bulk water)
- Fast dynamics (picoseconds): Under-bonded L3 molecules (no analogy in bulk water).

This final example demonstrates the extent to which diffusion mechanisms in catalytically relevant systems can be dissected using QENS. Mamontov pointed out that QENS is applicable to many such problems.

Following Mamontov's presentation, and in response to queries arising in the discussion, Ken Herwig presented a brief description of the factors relating to sample requirements and measurement time considerations for SNS instruments. These are summarized in Table 2.



**Table 2. Sample and measurement time considerations for SNS instruments**

Instrument	Capability	Max. Beam size	Time required	Status
POWGEN	Diffraction	14 x 40 mm <sup>2</sup>	1 h for 500 mg*	Available
NOMAD	PDF , liquid diff.	10 x 10 mm <sup>2</sup>	1.2 h for 100 mg	Available
TOPAZ	Diffraction	<sup>†</sup> 1 mm <sup>3</sup>	2-3 days for data set	Available
BASIS	QENS	30 x 30 mm <sup>2</sup>	12 h for 0.2 mmol H	Available
SEQUOIA	IINS	50 x 50 mm <sup>2</sup>	4 hr for 1 mmole H	Available
VISION	IINS, diffraction	30 x 50 mm <sup>2</sup>	12 h for 0.05 mmol H	2012

\* When POWGEN builds out to 50% of its detector complement, this will change to 1 hr for 100 mg.

<sup>†</sup> Volume of the single crystal sample.

## 2.3 Structural Characterization of Catalysts and Catalytic Materials

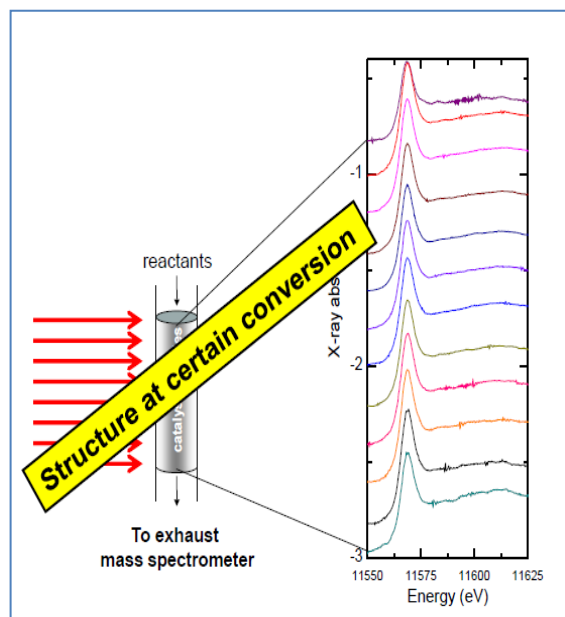
This session focused on the use of neutron techniques to perform static or time-dependent studies of structure. As was highlighted in Thiyagarajan's opening remarks, an important aspect of neutron scattering is the ability to probe low mass, "difficult" atoms in the presence of more massive atoms, e.g. hydrogen in metal-organic frameworks (MOFs). This ability to feature low-Z materials is of interest in many materials and conditions of catalytic interest, for example, (1) in low-Z catalytic materials—such as supported metals, oxides, nitrides, sulfides, phosphides, graphene, graphane, graphite oxide, CN, microporous and mesoporous materials—under catalytic or electrocatalytic reaction conditions; (2) in inorganic precursor materials—such as nitrates, phosphates, carbonates—under treatment or synthesis conditions; and (3) in surface species—especially molecular adsorbates, reactants, and products—under adsorption, electrocatalytic or reaction conditions. Structural features of interest may include crystallographic phases, composition, morphology, clusters, disordering, and defect structures. It may also include the structure of the active sites with a focus on local environment with elemental and oxidation-state resolution. In catalytic systems, it is of interest to obtain information about functional groups, active sites, bulk structural transformations, and defects on surfaces or within the bulk of catalysts. An important aspect, and a possible benefit of neutron studies, is the ability to discover or monitor structural changes that occur as reaction conditions change or as a function of catalyst deactivation. In this session, two speakers presented structural studies from two different points of view. The first highlighted the use of x-ray techniques for probing structure, both as applied conventionally and with cutting edge innovations. The second speaker described the use of total scattering methods in neutron

scattering, making comparisons with x-ray scattering, and provided several examples of how these methods can be applied in materials of catalytic interest.

Jeroen van Bokhoven of ETH Zurich presented a lecture (“Shining light on catalysis”) based upon his experience in using x-ray absorption spectroscopy (XAS) to understand the structure of catalysts. His introductory remarks focused on the need to understand structure in order to understand function. Because the structure of the active site may change during catalytic processes, it is necessary to look at the structure during a reaction. This is possible using x-ray absorption. From these methods, it is possible to get geometry, oxidation state, and density of empty states using x-ray absorption near edge spectroscopy (XANES) and to determine local structure and particle sizes with extended x-ray absorption fine structure (EXAFS).

Van Bokhoven described the beam line at which his team performs measurements, the details of a few different types of reactors used for x-ray absorption measurements, and the capabilities needed for a dedicated beam line for catalysis methods. Such capabilities might be needed for successful neutron experiments. He said a dedicated beam line is essential for success in catalysis experiments, described a few important issues related to reactor design (including the effects of conversion on changing reaction conditions), and emphasized the need for proper gas mixing and control systems. The beam line used by van Bokhoven has the unusual capability of using a fluorescent x-ray analysis and detection system to monitor fluorescence from various states above the excited core hole. Because the lifetime broadening of these lower binding energy states is less than the core hole, monitoring the intensity of this fluorescence yields XANES spectra with higher resolution, although they lose time resolution since the signal is weaker.

Van Bokhoven discussed discoveries made using these techniques. His team have found that they can resolve bonding sites of CO on platinum in XANES and quantitatively measure their relative numbers. Their detection scheme allows them to measure both the empty states above the Fermi edges (by x-ray absorption) and the filled states below the Fermi edges (by x-ray



emission). This combination allows following changes in the CO element- and spin-specific valence band structure induced by CO adsorption on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. Using a rapidly slewing spectrometer (quick EXAFS), they were able to watch oscillations in CO oxidation as a function of time and location on the reactor (Figure 6). These measurements distinguish between the platinum oxide that forms under oxidative swings (from white line intensity) vs CO adsorbed when the reaction swings toward CO poisoning, and resolve them in time and position. Since EXAFS data are obtained at the same time, they also measure variation in the Pt-O vs Pt-Pt neighbors, caused by the oscillating oxidation of the platinum, with a time resolution of about 100 ms.

**Figure 6. Measurement of XAS intensity in situ as function of position in reactor bed.**

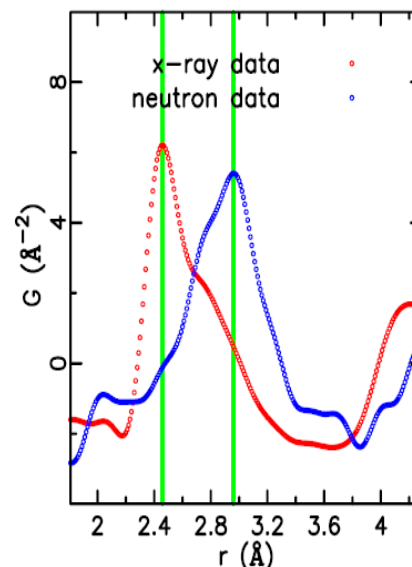
In the subsequent discussion there were questions and discussion relating to the following points:

- Are there limitations of x-ray absorption, e.g., to see low-Z elements, that could be complemented by neutron methods? It is possible to see hydrogen in x-ray scattering by its effects upon a catalytic metal or see adsorption by the effect of adsorbates upon the structure of the catalysts. For example, palladium forms a hydride that is completely different from palladium, so hydrogen can be seen in that way.
- One limitation of XAS is that penetration is not complete, so the substrate may make it difficult to see the metal of interest; therefore, the question is whether neutrons can help. It was mentioned that penetration may be a slight limitation, but there are examples where dilute metals can be measured at very low concentrations. Of course, other methods should be tried.
- Sample damage is important to consider in x-ray methods, especially with high-intensity focused sources. So the question was raised of the relative effect of neutrons on a sample.
- A question was raised about transition cross sections and claims that in some cases as particle size goes down, the x-ray white line intensity increases. Apparently, the intensity of white line depends upon the nature of the species. It was pointed out that what is probed is  $\rho$  density of states; changes in the number of neighbors can change white lines, but the edge jump should be quantitative. If the reference states are good, then principal component analysis is possible.
- Probing structure plus probing vibrational structure would give complementary information; this would be a useful example of combining techniques. Van Bokhoven mentioned that there is work in progress to combine IR and XAS, although it is “tricky” to do so.

Thomas Proffen of Los Alamos National Laboratory made a presentation on the subject of what is underneath Bragg peaks (“Characterizing complex materials using total scattering”). He cited his group’s Web site as a source of additional information (<http://totalscattering.lanl.gov>). Proffen’s initial point was that Bragg scattering provides the “average” structure of a material. In extreme cases, this may not be representative of any part of the sample. An example he cited is a material with a fixed number of vacancies in which the vacancies are clustered or distributed randomly; the distributions may be quite different in different areas, but the Bragg peaks will look nearly the same. However, by considering the total scattering, including that between Bragg peaks, it is possible to observe differences due to short-range ordering. A total scattering measurement, or rather its Fourier transform (FT), can yield a histogram of the atom–atom distances in a sample, and the intensities will be weighted according to the average numbers of nearest neighbors. Using the resulting pair distribution functions (PDFs) combined with modeling, it is possible to get both short-range and long-range structures of samples. The experimental considerations for performing total scattering successfully include (1) the need for high  $Q_{\text{max}}$  information to avoid termination errors in the FT, (2) high resolution to resolve atom–atom distances at large distances, and (3) good counting statistics. It is often helpful to compare neutron PDF (nPDF) with corresponding PDF data collected using x-rays (xPDF). At Proffen’s Los

Alamos beam line, there is an agreement with Argonne National Lab's Advanced Photon Source whereby users allocated nPDF time can also obtain xPDF time.

Proffen provided examples to illustrate PDF methods. He showed a comparison of xPDF and nPDF for a Mg-Co alloy that illustrated significant differences due to differences in neutron vs x-ray cross sections; this difference was useful for analysis of the material (Figure 7). An important point is that PDF is useful for poorly ordered materials such as ammonium borate confined in MCM41. It was possible to detect the ordering of ammonium borate by x-ray diffraction at high loadings (crystalline state) but not at low loadings. PDF analysis gave information about how this material exists in this structure at low loading. In another material examined,  $\text{LaMnO}_3$ , there was an apparent contradiction because the same Mn–O bond distances appear to persist to high temperatures in the local structure, even though the Jahn-Teller distorted structure disappears. Use of nPDF revealed local atomic distortions, explaining the contradiction and leading to a better understanding of the electronic and magnetic properties of this manganite.



**Figure 7. Comparison between nPDF and xPDF reveals structural features in Mn-Co alloy.**

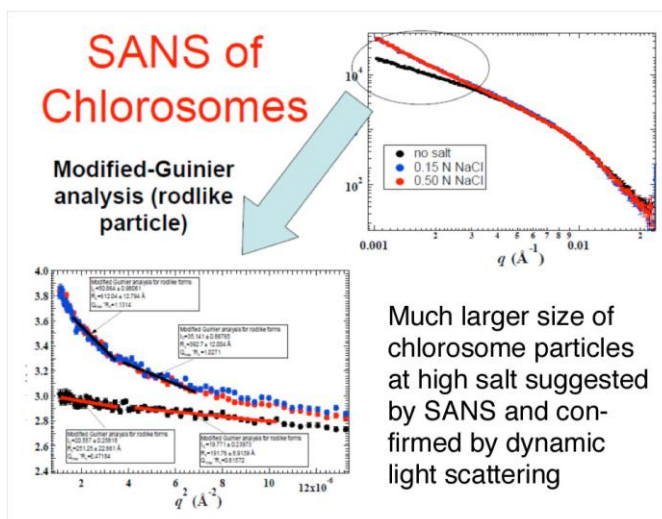
Proffen discussed applications for nanoparticle research, a subject of great importance to catalysis. For nanoparticles, an additional problem is that the Bragg peaks are broad because of the small particle size, complicating Rietveld analysis. Therefore, it is impossible to distinguish between two different models for the structure. The use of PDF coupled with modeling using the program “PDFgui” permits including size effects. In studies of nanoparticles of  $\text{BaTiO}_3$ , the PDF can be modeled as bulk  $\text{BaTiO}_3$  with a form factor for the limited shape. Adsorbates on nanoparticles can be seen by nPDF, allowing the possibility of determining bonding sites on nanoparticles. An example was given in which the structure of benzyl alcohol on  $\text{BaTiO}_3$  could be obtained from modeling of nPDF. PDF has also been used to study gold particles. Proffen listed the types of information that can be obtained from total scattering measurements, including particle size distribution, variation in adsorbed ligands, ligand–ligand interactions and ligand floppiness. His planned future work includes core-shell particles and refinement; the expectation is that these studies can aid in understanding anisotropic shapes and complex architectures. He emphasized that progress will require performing experiments in which the limits and capabilities of the methods can be explored.

## 2.4 Probing Biocatalysis by Neutron Scattering Methods

An important aspect of catalysis that can be addressed using neutron methods is studies of structure and function in biocatalysis. A Grand Challenge in catalysis is to explore how to create artificial catalysts that can mimic biological systems and what can be learned from such

biological systems. This approach can lead to creative ways to design new catalysts inspired by natural systems and allow us to move away from traditional metal catalysts. The session therefore focused on biocatalysis and on high-order problems in biocatalysis, including bio-energy applications. A goal was to provide a perspective on the potential for studying biological systems using neutron methods. This session was chaired by Dean Myles and involved contributions from two speakers, Robert Blankenship of Washington University ("Neutron scattering studies of photosynthetic energy transduction complexes) and Paul Langan of Los Alamos National Laboratory ("Neutrons for bioenergy").

Blankenship discussed photosynthetic systems, including light harvesting antenna systems. Blankenship is a leader of an Energy Frontier Research Center (the Photosynthetic Antenna Research Center, or PARC) that seeks to *understand the basic scientific principles that underpin the efficient functioning of the natural photosynthetic antenna system as a basis for manmade systems to convert sunlight into fuels*. PARC is built around three scientific themes involving a progression from purely natural, to hybrid, to purely artificial antenna systems. He categorized how photosynthetic energy storage systems work: light harvesting by the antenna system and transfer of energy to a reaction center for electron-hole separation. He showed examples of the large number of known antenna complexes and discussed briefly the process of excitation and transfer that occurs in them. He also gave an example of how these components are incorporated in a purple bacterial membrane. Blankenship also discussed the basic structure of the photosystem of green sulfur bacteria, which contains a chlorosome antenna system. To further study this system, PARC's scientists have constructed a biohybrid system composed of TiO<sub>2</sub> nanoparticles that have the chlorosome antenna complex attached. Excitation of the attached complex leads to electron injection into the TiO<sub>2</sub> support, creating essentially the bio-equivalent of a dye-sensitized solar cell. Blankenship described briefly how these are constructed using an electrospray process for depositing the chlorosome. As a part of this project, Blankenship and co-workers conducted experiments at ORNL using SANS to probe the chlorosomes. Using contrast variation by isotope matching, they obtained Guinier plots that fit well to the rod-like shape of the chlorosomes. They also performed studies to explore the stability of the complexes and the effect of salt treatments. Adding salt to these chlorosomes does not affect the absorption or the fluorescence spectrum, but SANS and dynamic light scattering show dramatic changes that imply big changes in the particle size (Figure 8). Analysis of the SANS data shows that the salt induces an aggregation of the chlorosomes.



**Figure 8. SANS data of chlorosomes demonstrate the aggregation that occurs upon treatment with salt.**



Following the talk, participants discussed why the chlorosomes aggregate and how changing the hydrophobicity of the solvent can change the solvation and aggregation. A question about how the membranes can have such high photoefficiency brought out that somehow these systems can avoid self-quenching processes, even though they are highly concentrated. The reason is related to the oligomeric structure, a subject of possible future study. There were also questions and discussion about the base plate in the native complex and about pigment proteins located there. The discussion turned to the logistics of performing SANS. In some cases, a few days are required to collect a data set; 6 to 8 hours may be needed to collect a SANS spectrum. Fortunately, since cells can make large numbers of the chlorosomes a fair amount of material is available for measurements, typically a few milligrams. A comment noted that it may be possible to use the time structure of the neutron beam to perform a pump-probe experiment to learn more about such systems.

Langan, a researcher in the Bioenergy and Environment Science Group at Los Alamos, noted his group's capabilities in using neutron diffraction to probe proteomics and protein crystallography (see <http://biofuels.lanl.gov>). Most of their work is concerned with biocatalysis. He discussed examples of the use of neutron diffraction in combination with other techniques such as x-ray diffraction, nuclear magnetic resonance (NMR), and modeling to probe and engineer biocatalytic processes. Because of the need to complement neutron studies with other measurements, he values and seeks partnerships with other labs and central facilities. Langan's talk provided examples from three important challenge areas: (1) conversion of lignocellulosic biomass to biofuels and bioproducts, (2) carbon transport in producing biofuels and bioproducts from algae, and (3) environmental decontamination, sensors, and carbon sequestration.

His first example concerned biocatalysis for conversion of cellulosic biomass to fuels. It is difficult to make this conversion because it is difficult to hydrolyze crystalline cellulose. There may be some gains in using enzymes for this hydrolysis. Approaches involve systems biology and metabolic engineering approaches to find new enzymes to enable xylose fermentation. Langan's approach is to work out in detail the catalytic mechanism of how the enzyme works and then use this information to re-engineer the enzyme so it can work in yeast. Xylose isomerase has been studied by x-ray crystallography and its structure described, but the motion of the protons has not been understood. Neutrons can probe the hydrogen and its motion. Langan's team showed how the action of the enzyme allows lysine to pull off a proton during the catalytic reaction. Results of neutron crystallography give snapshots at different steps in the reaction pathway, but a quantum mechanics approach is required to fully characterize the reaction pathways, transition states, and energy barriers that connect these different stages. Langan showed movies of the reaction resulting from these simulations. His team is in the process of using these results to reengineer xylose isomerase for use at low pH.

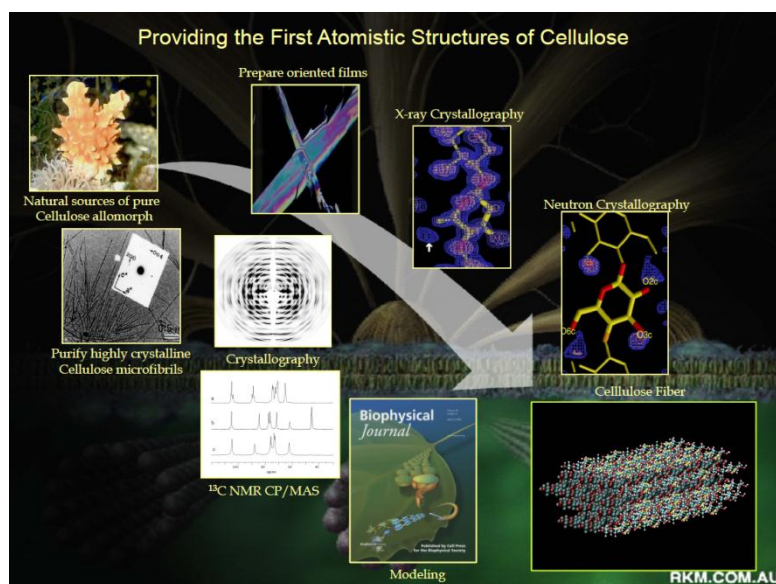
Langan also discussed using information from neutron crystallography to reengineer the active sites of enzymes. The idea is to change the stereochemistry of the binding pocket to stabilize an intermediate in a catalytic mechanism. He noted this approach has been used to study DFPase, an enzyme for biocatalytic activity against certain organophosphorous pesticides and nerve agents. His team has used it to study an enzyme called carbonic anhydrase (CA) to help with CO<sub>2</sub> intake and metabolism in algae. This enzyme interconverts CO<sub>2</sub> with carbonates. The idea is

to reengineer the CA for enhancing algae growth. Langan first described the reaction pathways in CA. The location of the protons was not well-known, even though the proton transfer process is the rate limiting step and is pH sensitive. They combined neutron measurements with  $^{13}\text{C}$  NMR to get static and dynamic pathways. It was crucial to co-optimize two different functions of the enzyme, and with this approach they have achieved significant improvements in algae growth.

In a third example, Langan discussed a process and an enzyme for hydrolysis of cellulose. His group has been working with a process called AFEX for conversion of cellulosic biomass. The goal is to understand how structural changes occur under the processing conditions. They used neutrons to determine atomistic structures of cellulose, in particular to determine the location

of the hydrogen (Figure 9). This required using both x-rays and neutrons to describe the full structure and then using modeling and NMR to characterize the dynamics. Using this approach, they have fine-tuned the AFEX process.

Langan emphasized the importance of combining techniques to probe the structure of biomass and biocatalysts and of using the information both to redesign enzymes to improve their catalytic capability and to manipulate the substrate (biomass) to enhance its susceptibility to biocatalysis. He offered the opinion that progress



**Figure 9. Use of complementary techniques, including neutron crystallography, leads to improved understanding of structure of cellulose.**

requires easy and simultaneous access to multiple “experimental platforms” because *techniques complementary to neutron techniques are essential*. Similarly, improved access to large-scale, modern computing facilities and expertise for modeling and simulation are necessary.

During the subsequent discussion several points were raised.

- A commenter reiterated that it is impossible to improve on an enzyme if you don’t know what is limiting its activity and complimented Langan on his approach to understanding cellulose and lignocellulose and paying attention to the structure of both the enzyme and the substrate. It was mentioned that one reason that biocatalysis community does not pay attention to the substrate is that it is soluble in water.

- A questioner pointed out that all three examples discussed were reaction systems that are thermodynamically "easy" (although DFPase is not easy). Langan mentioned that one benefit of the systems studied was that it is possible to grow large crystals of the systems of interest.
- A participant asked the size of the computer platform used and the breakeven point needed to make a contribution. Langan answered that the results shown were obtained using a small cluster but it took weeks to produce the movie that was shown. It was necessary to look out to 15 Å away from the active site; otherwise, the computations did not converge. To do such studies well would require petascale computing. But so far it has been difficult to code for such computers and to get access to them at Los Alamos (because these computers have been committed to solving national security problems).
- A participant—noting that the presented strategy is to combine neutrons and x-rays to obtain crucial information about catalytic function—asked how much certainty is sacrificed by using only x-rays and what neutron studies provide about "candidate" positions for hydrogen. Was hydrogen found where it was expected and could hydrogen locations not be "guessed" sufficiently? Langan responded that neutrons were essential. Typical previous work would lead to possibilities of mechanisms that depend on hydrogen positions. When positions were finally determined, there were always surprises, and the results were not what was expected. This means also quantum mechanics modeling is necessary to ensure that results are connected to function. Even x-ray studies refined to < 1 Å resolution did not determine all of the locations. It is best to have detailed, high-quality x-ray results before performing neutron measurements. Langan suggested that there should be joint portals for x-ray and neutrons, allowing essentially simultaneous beam time.
- It was pointed out that hydrogen atoms can be found in x-ray results, but generally these are not the interesting mobile ones. All work has previously been performed on the instruments used by Langan. The beam lines and increased flux at SNS will help improve this situation considerably.

## **2.5 Modeling of Catalysts, Catalysis and Neutron Experiments: A Crosscutting Activity**

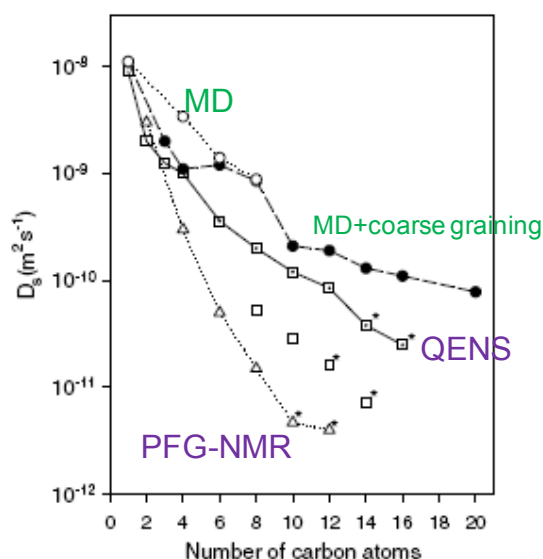
It is widely recognized that interpretation of most neutron scattering experiments requires computational modeling. Modeling of neutron experiments includes methods to interpret and extract quantitative information from QENS, IINS, and SANS data and the reverse process of predicting quasielastic and inelastic scattering response from first principles computations on catalytic systems. Therefore, workshop organizers thought it essential to highlight computational interpretation of neutron scattering experiments. Speakers were expected to present concepts, methodologies, and examples for modeling catalytic systems and tie these directly to the types of computations needed to interpret the scattering experiments. The goal is to introduce catalyst practitioners to the types of problems that can be addressed by neutron methods and see how computation contributes to analyzing the results. (Computational approaches are also a major component of predicting reaction pathways and properties of

catalytic systems for comparison with catalytic measurements, as is well known to the catalyst practitioners. However, it was not the goal of this session to explore the latter aspect.)

Presenters in this session were David Sholl from Georgia Tech and A. J. Ramirez-Cuesta from the ISIS Facility at Rutherford Appleton Laboratory.

The primary subject of Sholl's talk ("Combining theory and neutron scattering to understand molecular diffusion in porous materials") was molecular diffusion. He started by describing three model systems for study: crystalline zeolites, MOFs, and porous carbon. Because these catalytic materials have high surface areas, they concentrate chemical species, and these particular materials have well-defined catalytic sites. They may exhibit "shape selectivity" that can lead to high selectivity in catalytic reactions. This selectivity arises in part as a result of selective transport due to different diffusion rates for different molecules. It is possible to use computational modeling to describe these porous materials, including density functional theory (DFT) for modeling quantum chemistry for local interactions and molecular dynamics (MD) simulations for examining them on a larger scale ( $10^3$  to  $10^5$  atoms). The latter requires parameterized, empirical force fields. Diffusion is very sensitive to force fields, and diffusion probes more of the force field than just at the zero point. Sholl discussed self-diffusion, which is "easy" to compute and can be probed by NMR and QENS; and mass transport (Fickian) diffusivity, which also can be probed by QENS. Incoherent scattering measures self-diffusion and coherent scattering measures transport diffusivity. Sholl went on to compare the time scales for MD and neutron experiments. He showed that, because of computational limitations, MD can work only to find diffusion coefficients  $>10^{-6}$  cm<sup>2</sup>/s; whereas in liquids, the diffusion coefficient is typically  $10^{-5}$  cm<sup>2</sup>/s. Therefore, MD can work well on liquids. Similarly, the relevant time and distance scales for neutron methods are well matched to the MD time and length scale, making neutron spin echo, backscattering, and time-of-flight methods well suited for measuring and modeling diffusion. He provided equations describing the relation between the diffusion constant and the scattering functions and pointed out that each model needs to specify a description of the jump distances (fixed or a distribution).

Sholl described eight examples of diffusion results in which molecular dynamics modeling was done and compared directly with experimental measurements by QENS and NMR. In his first example, he showed the effect of alkane chain length on self-diffusion of n-alkanes in silicalite. This example demonstrates good agreement between coarse-grain MD and QENS measurements (see Figure 10). NMR results differed from QENS results, a difference that Sholl attributed to difference in the time scales and therefore different diffusion lengths. NMR samples diffusion lengths on the order of a micron, whereas QENS samples diffusion lengths on the order of a nanometer. Why these distances matter is a point for debate, but a commonly held hypothesis is that the longer diffusion lengths



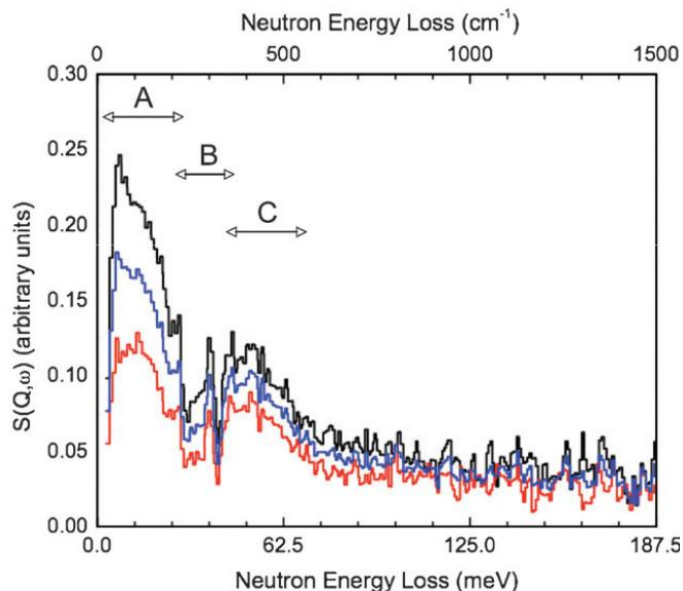
**Figure 10. Comparison of MD with QENS results of self-diffusion of hydrocarbons in silicalite.** [Jobic and Theodorou, *Micro. Meso. Mater.* **102** (2007) 21]

sampled by NMR are more affected by defects in the crystals. Another example involved the transport diffusion of CO<sub>2</sub> in an MOF, MIL-47(V). Since CO<sub>2</sub> scatters neutrons coherently, only transport diffusion is accessible. This experiment is notable because the MOF contains hydrogen in the linker molecules, whose incoherent scattering interferes with the measured coherent scattering from CO<sub>2</sub>. Nevertheless, the experiment worked and the CO<sub>2</sub> diffusion coefficient was measured as a function of CO<sub>2</sub> density. The obtained diffusivities are similar to those of liquids, although the MD results were 5–10 times smaller than the measured values. Sholl discussed diffusion of H<sub>2</sub> and D<sub>2</sub> in porous carbon, a study that shows quantum effects at low temperature and CH<sub>4</sub> diffusion in porous carbon and features QENS data obtained at SNS. The latter study also made use of SANS to probe filling of the pores vs methane pressure. The biggest difficulty in performing MD in this system is getting a good structural model of the carbon material. Finally, Sholl showed examples to describe diffusion in mixtures, including self-diffusion of CH<sub>4</sub> in CO<sub>2</sub> or in C<sub>4</sub>D<sub>10</sub>. He stated that progress will come from working at the intersection among materials synthesis, neutron measurements, atomistic simulations, and complementary experiments. He sees opportunity arising in studies of interesting new materials with unusual properties (e.g., zeolite DDR), diffusion in flexible materials, diffusion in mixtures, and hierarchical materials in which diffusion involves difference with size scaling.

Ramirez-Cuesta of ISIS (“The power of inelastic neutron scattering: Vibrational spectroscopy of hydrogen, applications to catalysis”) primarily discussed using IINS for extracting vibrational and phonon information about solids and adsorbates in catalytic systems. He pointed out that the way an object vibrates reflects its structure. After reviewing the energy transfer and length scale probed during various inelastic neutron scattering regimes and comparing Raman, IR absorption, and IINS experiments, Ramirez-Cuesta described vibrations of normal modes and extracted them from the force constant matrix. Key features of neutron scattering are that transitions are proportional to the amplitude of motion and the cross section of the nuclei, and that there are no selection rules. (P. C. H. Mitchell, S. F. Parker, A. Ramirez-Cuesta, and J. Tomkinson, *Vibrational Spectroscopy with Neutrons With Applications in Chemistry, Biology, Materials Science and Catalysis*, vol. 3 in *Neutron Techniques and Applications*, World Scientific Publishing Company: London, 2005). In general IINS is performed at low temperature, e.g. at 15 K, because the thermal excitation will pile intensity into the overtones and combination modes, complicating interpretation. However, the details are dependent on whether the experiment is performed on an indirect geometry instrument (such as TOSCA or VISION) or on a chopper machine on which the incident energy can be varied (such as SEQUOIA or ARCS).

To interpret IINS spectra, calculations are effectively a necessity. Ramirez-Cuesta described use of the DFT code CASTEP to compute IINS spectra, but he stated that any calculation that gives the eigenvectors and frequencies can be used. (A. J. Ramirez-Cuesta, “CLIMAX 4.0.1, The new version of the software for analyzing and interpreting INS spectra,” *Computer Physics Comm.* **157**, 226–238 2004). In a calculation on MgH<sub>2</sub> he showed how inclusion of first- and second-order overtones and combination bands is important for fitting IINS spectra at higher values of neutron energy loss. He also gave examples of the importance of sampling a large enough grid in k-space in the simulation to obtain agreement with the experimental spectrum. The hydrogenation of nanostructured sodium silica gel into (Na SG into NaH SG) under mild conditions was presented as a use of inelastic scattering and modeling to determine the size of

nanoparticles of NaH formed, as well as an absolute determination of the efficiency of the conversion reaction. (A. Sartbaeva, S. Wells, M. Sommariva, M. Lodge, M. Jones, A. Ramirez-Cuesta, and G. Li, et al. "Formation of crystalline sodium hydride nanoparticles encapsulated within an amorphous framework," *J. Cluster Science*, **21**(3), 543–549, 2010). This effect of k-space sampling was further illustrated by additional IINS measurements of H<sub>2</sub> adsorption on Raney nickel; H<sub>2</sub> dissociates on the metal surface. This mechanism was modeled as dissociated hydrogen adsorption on Ni(111), Ni(110) and Ni(100) surfaces. The correspondence with the experimental data demonstrates that for the particular sample, 80% of the signal is due to the Ni(111) surface. An example demonstrating studies of molecular adsorption was IINS studies of NH<sub>3</sub> adsorbed in zeolite A. (A. G. Seel, A. Sartbaeva, A. J. Ramirez-Cuesta, and P. P. Edwards, "Inelastic neutron scattering of Na-zeolite A with in situ ammoniation: An examination of initial coordination," *Phys. Chem. Chem. Phys.* **12**, 9661–9666, 2010). Spectral components due to librational, vibrational, and rotational modes of the NH<sub>3</sub> bonded to an extra-framework Na<sup>+</sup> cation were observed and their contributions to the IINS spectra were examined using ab-initio calculations (Figure 11).



**Figure 11. Three modes of motion for NH<sub>3</sub> in zeolite.**

The catalytic hydrogenation of organic molecules as hydrogen storage vectors was also presented, illustrated by a series of studies involving mass spectrometry, NMR, and the thermodynamics effects that is fully backed up by full ab-initio thermodynamic calculations. (K. M. Eblagon, D. Rentsch, O. Friedrichs, A. Remhof, A. Zuettel, A. Ramirez-Cuesta, and S. C. Tsang, "Hydrogenation of 9-ethylcarbazole as a prototype of a liquid hydrogen carrier," *Int. J. Hydrogen Energy* **35**(20), 11609–11621, 2010). IINS results were presented to determine the most likely species to be formed as intermediates in the reaction.

Ramirez-Cuesta revisited the adsorption of CH<sub>3</sub> on Pd, a system discussed earlier by Peter Albers, and presented results in which classical mechanics and force field fitting were used to match the experimental spectrum. He concluded that modeling is a vital part in the interpretation of catalysis studies with IINS. Catalysis experiments with neutrons are particularly demanding with many pitfalls. Careful experimental design and the proper sample environment are very important for success.



### 3. Breakout Sessions

A guiding principle of this workshop was there would be extensive discussions leading to description of ideas for research proposals that could be carried out at the neutron facilities at ORNL, especially the SNS. With this in mind, the workshop broke out into three working groups. Their charge on the first day was to identify Grand Challenge questions that may be addressed with neutron scattering methods. The breakout groups were asked to consider the following points:

- **Consider, discuss and prepare a working list of Grand Challenge problems.** Examples of Grand Challenge problems include understanding mechanisms and dynamics of catalyzed transformations, carbon dioxide reduction to fuels or water oxidation, and understanding the chemistry of biomass processing at high temperature.
- **Consider kinds of information that can be obtained from relevant neutron scattering methods.** For structure these may be neutron diffraction, IINS, pair distribution methods, and neutron reflection. For dynamics, they may be IINS and QENS. Draw on the expertise of assigned neutron experts. Complementarity with x-ray or other methods may be considered to determine how a combination of methods leads to new understanding.
- **Consider what types of materials and systems can be uniquely probed by neutrons.** For example, what breakthroughs can be achieved in soft materials and participation of hydrogen in catalytic processes? What is the implication of magnetic scattering in probing free radicals or paramagnetic centers in catalysts?
- **Reconsider the list of Grand Challenges.** How can inroads into these questions be made using neutron methods? What are specific experiments that could be undertaken?

On the second day, results of the first breakout session were presented to the assembled workshop participants. The presentations are available on the workshop Web site <http://neutrons.ornl.gov/conf/NandC2010/talks.shtml>. Following the session “Modeling of Catalysts,” the workshop broke out into the three groups, with the following charge:

- **Identify 2 or 3 specific experiments** that could be addressed by a particular neutron scattering technique. A leader and working group were expected to emerge for each experiment.
- **Identify the instrument that is needed to** perform the neutron measurements. This may involve connecting to the SNS Web site and help from assigned neutron experts.
- **Discuss the sample environments needed** and limitations of temperature, pressure, and other conditions.
- **Discuss needed computational support** for interpretation of the expected results.
- **Draft basic elements of the proposal.**

The following section details the thoughts and outcomes of the three breakout groups. The results of both days are combined.

### 3.1 Dynamics Breakout Sessions

The workshop's fundamental challenge was to address how neutron science can play a role in the field of catalysis; specifically, how can SNS help elucidate reaction mechanisms, explain diffusion, describe pore chemistry, explain molecular diffusion (such as jump diffusion), or even look at unexplored territory, such as catalyst synthesis. Traditionally catalyst systems are characterized using XRD, XANES, EXAFS, Fourier transform infrared, and Raman. Neutrons, however, possess physical properties to aid in understanding the structure and dynamics of materials at the molecular level; thus SNS may provide the capability to add to the understanding of materials that are difficult to interpret by other techniques, may provide information that other techniques cannot provide at all (such as movements of atoms during catalytic reactions), or may be used as a complementary technique in addition to other characterization tools.

The marriage between neutron science and catalysis has not yet been probed extensively. It would be prudent to begin with elementary ideas based on what catalyst scientists are interested in exploring, such as diffusion and surface characteristics. Exploring well-known catalyst systems such as zeolites (which have crystalline regularity) or pillared clays (representative of two-dimensional diffusion) that can be used to explore the extent of confinement on diffusional processes would be an ideal starting point. A particular interest in describing these systems is understanding diffusional chemistry in a porous system. Possibly neutrons could provide relative spatial qualitative information, such as the difference in the time molecules spend residing at the mouth of a pore versus the time spent inside a pore. Could neutrons describe defects in a surface, or even distinguish the outside surface from the internal surface? Other interests would explore surface characteristics that many other spectroscopy techniques have difficulty in explaining, such as what is *on* the surface, or how is it coordinated? What are the distances between catalyst sites, or how are materials laid down on a surface—monodentate, bidentate, etc. Can the rate of catalyst adsorption, rate of exchange, or desorption be quantified? It is evident that to probe these dynamic relationships with neutrons, QENS (useful for small indirect distances) or NSE would be ideal platforms.

Working with SNS would potentially require special sample holders, instrument setups, or even staging areas for sample preparation. It would be beneficial to have SNS instrument engineers work alongside the experimentalist to help design conditions needed for catalyst studies, for example, designing cells to operate at realistic temperature and pressures. The requirement for large sample sizes is also a concern—the amount of catalyst required seems out of reach for some neutron studies. Working together, neutron and catalysis scientists could come to a reasonable solution. Another goal would be to use computational models that could complement neutron studies, maybe through spectral interpretation, or even theoretical models in comparison with experimental results.

Some immediate obtainable goals were identified in this group. For example, the diffusion of hydrogenous molecules in model systems; diffusion of hydrogen on a surface (spillover), i.e., what role can be gleaned in hydrogenation/dehydrogenation reactions; molecular diffusion mechanism (jump diffusion) (could look at average jump distance and how that correlates with



distance between cations in a zeolite). It is also possible to label models with deuterium for coherent scattering experiments as well to aid in such experiments.

### **Identify possible experiments**

Several possible experiments were discussed at the conclusion of the dynamic breakout session that seemed like viable approaches to probing the dynamics of catalyst systems using neutrons. (1) Look at the dynamics and interactions of self-assembled monolayers. For instance, study the interaction between the sulfur head group of a ZSM-5 tethered with alkyl thiol with gold on the surface. (2) Study the growth of particles on a substrate such as a silicon wafer for self-assembled monolayers. (3) Look at the chemical reaction of ethylene to ethylidyne on Pt/Pd particles. Look at the how the molecules associate/dissociate from the surface. Another possibility: detect reactions of intermediates, which is difficult, if not impossible, because of the time-scale resolution (ms-s) for dynamic measurements. This is where the use of designed quench experiments could provide assistance. Neutron spectrometers for inelastic and quasi-elastic measurements are capable of carrying out in-situ temperature-dependent studies, typically in an aluminum sample holder under a helium atmosphere. (4) Engineer a quench experiment looking at the interaction of propylene on metal exchanged ZSM5 (for example, A. Bell, et.al., *J. Catal.*, 255, 153, 2008).

## **3.2 Structural Characterization Breakout session**

### **Identify Grand Challenge structure topics**

*Characterization of hydroxyl groups on oxide supports:* There is a need for progress in understanding the relationships between catalyst structure and performance, particularly in metal-support systems. Hydroxyl groups are known to be anchor centers for the active metal species. Therefore, identification of their location and ordering would be of great interest in the field, since conventional spectroscopic techniques fail to identify the location and ordering of OH-groups and defects present in such systems.

*Synthesis and characterization of zeolites:* It has not been well understood how the synthesis process occurs in the highly ordered crystalline zeolite materials, and the identification of acid sites in zeolites continues to be a challenge. The development of synthetic principles for the highly ordered zeolitic materials is still a central theme in catalysis research. New nanostructures should incorporate elements of oxide frameworks or inorganic–organic systems and should contain multiple functionalities. Advances in this area of catalyst synthesis must be accompanied by breakthroughs in characterization methods that would allow identification of detailed structures and acid centers that act as ligands and can influence the properties of an active metal center. This is a similar issue to that raised when investigating the hydroxyl groups on oxide supports.

*Metal-support interface characterization:* In many reaction systems, it is believed that the reaction centers are located in the metal-support interface. Therefore, characterization of this interfacial structure is needed under static and time-dependent conditions. In-situ scattering

and imaging tools need to be developed to allow time-dependent monitoring of catalyst structure of metal clusters and nanoparticles at the nanometer level.

*Investigation of hydrogen spillover and reactions involving hydrogen and carbon–hydrogen bonds:* Although hydrogen spillover is a mechanism well documented in heterogeneous catalytic reactions, it is difficult to obtain direct proof. Neutron techniques would be particularly useful in detecting hydrogen atoms migrating on metal nanoparticles. The same would be applied for reactions involving carbon–hydrogen bonds and migration of hydrogen atoms during reaction.

*Characterization of structural changes during catalytic reaction:* Measurements under catalytic reaction conditions are challenging because the temperatures and pressures are often high. Therefore the high penetration of neutrons can be of great advantage. Probe reaction systems were discussed, such as water gas-shift reactions and CO oxidation.

### **Identify relevant systems/materials/environments**

- *Well-defined metal oxide nanoparticles:* The high surface area and ordered structure would enable a sufficient atomic fraction of the elements of interest to be measured by neutron techniques. Oxide nanoparticles would serve as models for the issues related to identification of hydroxyl groups on oxide supports.
- *Organometallic complexes, molecular clusters, and nanoparticles hosted in zeolites:* Highly ordered and high-surface-area materials such as mesoporous silica, MOFs, and zeolite materials (faujasite, for instance) would be ideal models for investigation and design of new nanostructure functionalities.
- *Nanoparticles with narrow size distribution:* Nanoparticles such as platinum in sizes between 1 and 2 nm supported on high-surface-area materials would make interesting model systems because of their uniformity of size. They would enable the creation of models for resolving structures by neutron techniques.
- *Carbon-based materials:* One of the drawbacks of carbon-based materials research is the lack of fundamental understanding of their physical and chemical characteristics. Advances in this area require the development of suitable characterization techniques, and neutron techniques could play a role. For instance, activated carbons and carbon-supported metals are interesting materials for liquid-phase hydrogenation and applied in biofuels. It is anticipated that neutron scattering can be a powerful technique for the study of these catalytic systems.
- *Catalytic probe reactions:* Low-temperature CO oxidation, water-gas-shift, and hydrogenation reactions would be systems of interest. This would require routine gas handling, product and reactant analysis, temperature and pressure control, and compatible reaction cells.

### **Practical neutron science questions**

The available facilities at SNS and HFIR that would accommodate neutron techniques identified as important for unraveling catalytic structures—such as powder diffraction experiments,

inelastic neutron scattering, and small angle scattering—were discussed. The catalysis group was concerned with the characteristics of the beam lines (flux, energy resolution, spatial resolution) and the availability of beam time for catalysis science. Other practical aspects discussed were the following:

- *Existence of complementary techniques, such as XAS, infrared, Raman, and XRD:* In order to achieve fundamental, atomic-scale characterization of catalytic materials, there is a need to apply multiple techniques in concert either simultaneously or sequentially and with a control of the sample environment.
- *Need for sample preparation, gas handling capabilities, and product and reactant analytical instruments available for catalysis users:* Since neutrons are highly penetrative, it would be a great advantage to have in situ cells for high-pressure (1–100 bar) gas–solid and liquid–solid catalytic reactions.
- *Handling of irradiated samples:* Questions were raised about the sample conditions after the measurements, since the researcher often would like to perform other characterizations using the same sample. Concerns from the catalysis researches were related to the decay period, whether samples are usually returned to the users, and how they would be disposed of.

### **Identify potential experiments**

Most of the proposed potential experiments discussed during this session were directly related to the Grand Challenges identified during the previous day. Highlights of the discussion follow.

- *Hydroxyl groups on oxide supports:* This was proposed following the scientific question of identification of location and ordering of the hydroxyl groups which serve as anchor centers for the active metal species. The main discussion at this point centered on the practical aspects, i.e., the design and feasibility of such experiment. The main conclusion is that would be advantageous to use very high surface materials and model nanocrystalline oxides.
- *Organometallic complexes, molecular clusters, and nanoparticles hosted in zeolites:* Faujasite was identified as being a very good candidate for studying detailed structures and acid centers in zeolite-type materials. Part of the discussion revolved around the resolution requirements for a PDF analysis of this kind of material.
- *Carbonaceous species at the surface:* It was proposed that neutron techniques would be very useful to study coke formation and deactivation processes.
- *Biomass conversion applications:* Reactions such as dehydration would be good model systems. In this field, the investigation of the intermediates leading to coke formation was proposed.
- *Catalysis under pressure:* A lot of discussion focused on how to design an experiment to investigate how catalytic structures are modified under hydrogen pressure. An issue was raised of how to properly remove the gas-phase hydrogen contribution to the surface species. It was proposed to look at a given catalyst under a wide pressure range of hydrogen.

- *Carbon-based materials*: Characterization of activated carbons, mesoporous carbon, and other carbon-based supports and catalysts.

### 3.3 Biocatalysis Breakout Session

Neutron scattering, with its unique ability to provide both structural and dynamics information on a wide range of time and length scales, can address a range of problems in biocatalysis. The length scales that can be probed span from 1 to 10,000 Å, and dynamic processes that occur from femtoseconds to microseconds can be studied. Crystallography and solution diffraction can provide structural information down to the atomic level, while reflectometry and small-angle scattering can probe long length scales typical of supramolecular complexes. Similarly, neutron vibrational spectroscopy can characterize localized femtosecond vibrations; time-of-flight and backscattering can probe picosecond and nanosecond phenomena; and spin echo can probe dynamic processes out to the microsecond time scale. These capabilities, when combined with the nondestructive and highly penetrating nature of the neutron, make neutron scattering ideally suited to the study of complex biological systems. Further, neutron scattering is extremely sensitive to hydrogen and deuterium. As a result, the judicious use of selective hydrogen/deuterium (H/D) labeling opens new possibilities in the study of biological systems by providing a means of highlighting portions of an intact, functional whole.

The overarching goal of the biocatalysis breakout sessions was to address key scientific issues in biology using a *multiscale* approach that leverages resources unique to ORNL, namely the most powerful neutron sources and supercomputing resources in the world. Neutron scattering, a unique capability of ORNL, plays an integral role in the experimental approach, while the National Center for Computational Sciences at ORNL has some of the most powerful supercomputers dedicated to unclassified scientific research. In the first breakout session, the team identified the following Grand Challenges that it was felt were primed for scientific breakthroughs that will result in the gain of knowledge at an unprecedented level.

#### Grand Challenges

- Heterogeneous systems: catalytic conversion of biomass, cellulases
- Energy transduction: light-harvesting antenna systems
- Understanding the physiochemical basis for enzyme stability

#### Key experiments

A series of key experiments were proposed in the grand challenge areas:

- In situ real-time analysis of biomass enzymatic digestion: (the substrate-enzyme interface)
- Kinetics and dynamics of photo-responsive enzyme complexes
- Thermal activity and stability (kosmotropes, chaotropes, solvent effects)

The team drew up plans for several proof-of-principle experiments in some key areas identified earlier on at the workshop.

1. Improving enzyme thermal stability

Improving enzyme performance under industrial conditions requires that several factors be optimized at the same time: thermostability, pH optimum, reaction rate, and substrate specificity. Local protein unfolding will be studied by probing the rate of H/D exchange with neutrons. This H/D exchange pattern can be used to map out areas of local unfolding. Amino acids within areas prone to local unfolding could be point-mutated to help stabilize the protein so that it has a longer half-life and is more thermally stable. These mutant enzymes would then be biochemically characterized to investigate possible increases in thermal stability while also being assayed to ensure that the pH optimum, reaction rate, and substrate specificity are as desired. The first enzyme selected is a commercially important aldose reductase enzyme involved in xylose metabolism.

## 2. Crystal structures and modeling

Understanding how the structure, function, and dynamics of an enzyme system affect function through the catalytic steps of an enzyme pathway (or the dynamical effects of ligand binding or protein–protein association) remains a major challenge in molecular biophysics. We aim to achieve a detailed understanding of the physiochemical mechanisms through which key enzymes function. Neutron crystallography and spectroscopic data will be combined with computer simulation to obtain a fundamental understanding of the structure, dynamics, energetics, and thermodynamics governing the biocatalytic mechanisms and pathways involved in proton transfer in protein structures and larger functional assemblies. Of particular importance will be the role of leadership-class simulation in integrating and interpreting multiscale neutron data. The system sizes obtainable via leadership-class atomistic MD simulation will be sufficient to provide a framework for simultaneous interpretation of neutron scattering results from multiple instruments. Also, coupled cluster calculations performed with the NWChem package currently scale to approximately 200,000 cores and will be used to obtain accurate single-point energies on proton-dressed enzyme active sites.

## 4. Outlook and Recommendations

The goals of the Neutrons and Catalysis Workshop were as follows:

1. Bring leaders in the catalysis community together with experts in neutron scattering techniques to explore how Grand Challenge problems in catalysis can be explored using neutron methods.
2. Help users identify their own proof-of-principle experiments.
3. Educate potential users in the catalysis community about the opportunities, limitations, and availability of neutron methods for performing their own experiments.
4. Educate neutron scattering researchers and instrument scientists about the needs and interests of the catalysis community.
5. Position ORNL user facilities to enable world-class catalysis research.

Goal 1 was largely accomplished over the course of the workshop, and Goal 2 was initiated among those who attended the breakout sessions. Goals 3–5 are ongoing, and

recommendations for addressing them and for future expansion of neutron scattering methods among the catalysis community are as follows:

- Continue to develop personal contacts with catalysis researchers with the goal of generating user-submitted proposals. This goal can be facilitated through activism by individuals within the catalysis community and continued commitment from ORNL's Neutron Scattering Science Division. Special effort should be directed at ensuring that proposal calls, mailings, announcements, and research highlights related to catalysis and catalytic materials reach a wide distribution within the catalysis community.
- Education of prospective neutron scattering facility users could be facilitated by tutorial-type information available through links from the ORNL Web sites. Many potential facility users are confused or uneducated about the experimental constraints of beam lines, including the amount and configuration of sample required for a successful experiment and the typical interferences that can doom an experiment. How much sample is required? How thick should it be? What elements are invisible or swamp out the signal of interest? A booklet or table of neutron cross sections will not help a typical user as much as would a simple, easy-to-read narrative of experimental pitfalls and rules of thumb for carrying out a successful experiment in QENS, IINS, NSE, nPDF, or neutron diffraction.
- Most potential experimenters at neutron scattering facilities from the catalysis community are attracted by the *in situ* or *operando* types of experiments promised in neutron scattering. Yet few instruments currently permit even simple manipulations (*in situ* heating, reduction, or oxidation) during measurement, not to mention combining neutron measurements with other methods performed simultaneously. Such methods would require special sample holders, instrument setups, or even staging areas for sample preparation. It would be beneficial to have SNS instrument engineers work alongside experimentalists to help them design environments needed for catalyst studies, for example, cells to permit control of temperature, pressure, and gas composition within the sample holder.
- A visiting scientist program could help to build collaborations between the ORNL neutron facilities and the catalysis communities.
- Interpretation of neutron experiments frequently depends upon high-level computation. It is necessary to develop links between experimentalists interested in neutron measurements and researchers with the computational expertise to perform appropriate modeling and simulation to enhance understanding of the experiments.

Completion of these recommendations will put ORNL on the path to accomplishing the fifth goal of positioning ORNL user facilities to enable world-class catalysis research.

## 5. Acknowledgements

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## Appendix A Workshop Agenda

*Neutrons for Catalysis: A Workshop on Neutron Scattering Techniques for Studies in Catalysis*  
Oak Ridge National Laboratory, Spallation Neutron Source, Building 8600  
September 16-17, 2010, Iran Thomas Auditorium, Room A-103

<b>Thursday, September 16, 2010</b>	
7:15 am	Shuttle bus leaves Comfort Inn hotel
7:30	Registration; Breakfast available (Atrium)
8:00	<b>Introduction and Program Overview</b> <ul style="list-style-type: none"> <li>Michelle Buchanan, Oak Ridge National Laboratory</li> <li>Pappannan Thiagarajan, US DOE</li> </ul>
8:10	<b>Meeting Grand Challenges in Catalysis through Neutron Scattering Techniques</b> Moderators: Phil Britt, Ken Herwig <i>Each presentation will be 30 minutes with 10 minutes Q&amp;A</i> <ul style="list-style-type: none"> <li>Bruce Gates, University California at Davis, “Grand challenges in catalysis research: understanding catalysis at the atomic scale as a basis for design of catalytic structures”</li> <li>Juergen Eckert, University of California, Santa Barbara, “Neutrons as microscopic probes in heterogeneous catalysis”</li> </ul>
9:30	Break (Atrium)
9:45	<b>Probing Dynamics of Molecules in Catalysts Systems by Inelastic Neutron Scattering</b> Moderators: Steve Overbury, David Wesolowski <i>Each presentation will be 30 minutes with 5 minutes Q&amp;A.</i> <ul style="list-style-type: none"> <li>Peter Stair, Northwestern University, “Some Thoughts About Surface Hydroxyl Groups and Catalysis”</li> <li>Peter Albers. AQuRA, “Applications of Neutron Scattering and Chemical Industry Characterizations of Technical Catalysis from Operating Large Scale Plants, Hydrogen Species on Fuel Cell Catalysis”</li> <li>Eugene Mamontov, Oak Ridge National Laboratory, “What can we learn about the mobility of species in catalytic systems using quasielastic neutron scattering?”</li> </ul> <i>Discussion follows (40 minutes)</i>
12:10 pm	Lunch and open discussion (Atrium)
1:00	<b>Structural Characterization of Catalysts and Catalytic Materials</b> Moderators: Viviane Schwartz, Takeshi Egami <i>Each presentation will be 30 minutes with 5 minutes Q&amp;A</i> <ul style="list-style-type: none"> <li>J. van Bokhoven, ETH Zurich, “Shining light on catalysts”</li> <li>Thomas Proffen, Los Alamos National Laboratory, “Advanced Characterization of Materials using Total Scattering”</li> </ul> <i>Discussion follows (40 minutes)</i>
2:50	Break (Atrium) and Group Photo
3:00	<b>Probing Biocatalysis by Neutron Scattering Methods</b> Moderator: Dean Myles. <i>Each presentation will be 30 minutes with 5 minutes Q&amp;A</i> <ul style="list-style-type: none"> <li>Robert Blankenship, Washington University of St. Louis, “Neutron Scattering Studies of Photosynthetic Energy Transduction Complexes”</li> <li>Paul Langan, Los Alamos National Laboratory. “Neutrons for biocatalysis”</li> </ul> <i>Discussion follows (30 minutes)</i>
4:40	<b>Break-out Session I – Attacking Grand Challenge problems with neutron experiments</b> <ul style="list-style-type: none"> <li>Structure (SNS Iran Thomas Auditorium): Breakout facilitator: Mike Simonson, Breakout spokesman: Henry Lamb, Scribes: Viviane Schwartz, Ashfia Huq</li> <li>Dynamics (SNS Room C-152): Breakout facilitator: Phil Britt, Breakout spokesman: Rob Rioux, Scribes: Michelle Kidder</li> <li>Biocatalysis (SNS Room C-464): Breakout facilitator: Dean Myles, Breakout spokesman: Andreas Bommarius, Scribes: Leighton Coates</li> </ul>
6:30	<b>Reception, Dinner, and Tour of SNS (Atrium)</b>
8:30	<b>Buses depart SNS for hotel (SNS flagpole)</b>

<p style="text-align: center;"><i>Neutrons for Catalysis</i></p> <p style="text-align: center;">Iran Thomas Auditorium (Room A-103), Spallation Neutron Source, Building 8600</p> <p style="text-align: center;">Oak Ridge National Laboratory</p> <p style="text-align: center;">Friday, September 17, 2010</p>	
7:15 am	Buses depart hotel
7:30	Breakfast available (Atrium)
8:00	<p>Results of Break-out Session I</p> <ul style="list-style-type: none"> <li>• Dynamics (Robert Rioux, Pennsylvania State University) (10 minutes)</li> <li>• Structure (Henry Lamb, North Carolina State University) (10 minutes)</li> <li>• Biocatalysis (Andreas Bommarius, Georgia Institute of Technology) (10 minutes)</li> </ul> <p><i>Clarification and Q&amp;A (10 minutes)</i></p>
8:40	<p>Modeling of Catalysts, Catalysis and Neutron Experiments; A crosscutting activity</p> <p>Moderators: Peter Cummings, Bobby Sumpter. <i>Each presentation will be 30 minutes with 5 minutes Q&amp;A</i></p> <ul style="list-style-type: none"> <li>• David Sholl, Georgia Institute of Technology, “Combining theory and neutron scattering to understand molecular diffusion in porous solids”.</li> <li>• A.J. Ramirez-Cuesta, ISIS Facility, STFC, Rutherford Appleton Laboratory, “The Power of Inelastic Neutron Scattering: Vibrational Spectroscopy of hydrogen - applications to catalysis”</li> </ul> <p><i>Discussion follows 20 minutes)</i></p>
10:10	<p>Discussion of proposal preparation</p> <p>Dean Myles</p>
10:20	<p>Break-out Session II – P-o-p experiments, proposal preparation, crosscutting activities</p> <ul style="list-style-type: none"> <li>• Structure (SNS Iran Thomas Auditorium): Breakout facilitator: Mike Simonson, Breakout spokesman: Henry Lamb, Scribes: Viviane Schwartz</li> <li>• Dynamics (SNS Room C-156); Breakout facilitator: Phil Britt, Breakout spokesman: Rob Rioux, Scribes: Michelle Kidder</li> <li>• Biocatalysis (SNS Room C-152): Breakout facilitator: Dean Myles, Breakout spokesman: Andreas Bommarius, Scribes: Leighton Coates</li> </ul>
12:00 pm	Lunch, Closing Remarks and Wrap-up (SNS Iran Thomas Auditorium)
1:00	<p>CNMS Discovery Seminar (SNS Iran Thomas Auditorium)</p> <p>Simon Bare, UOP , LLC, “Development and Applications of an Program for in situ XAFS Studies for Catalyst Characterization at UOP”</p>
2:00	<p>Discussion of Workshop published output (SNS Room C-156)</p> <p>Speakers, spokesmen, facilitators (invitation only)</p>
2:10-5:00	<p>Preparation of Workshop Summary Report (SNS Room C-156)</p> <p>Session facilitators, spokesmen, scribes, others (invitation only)</p>

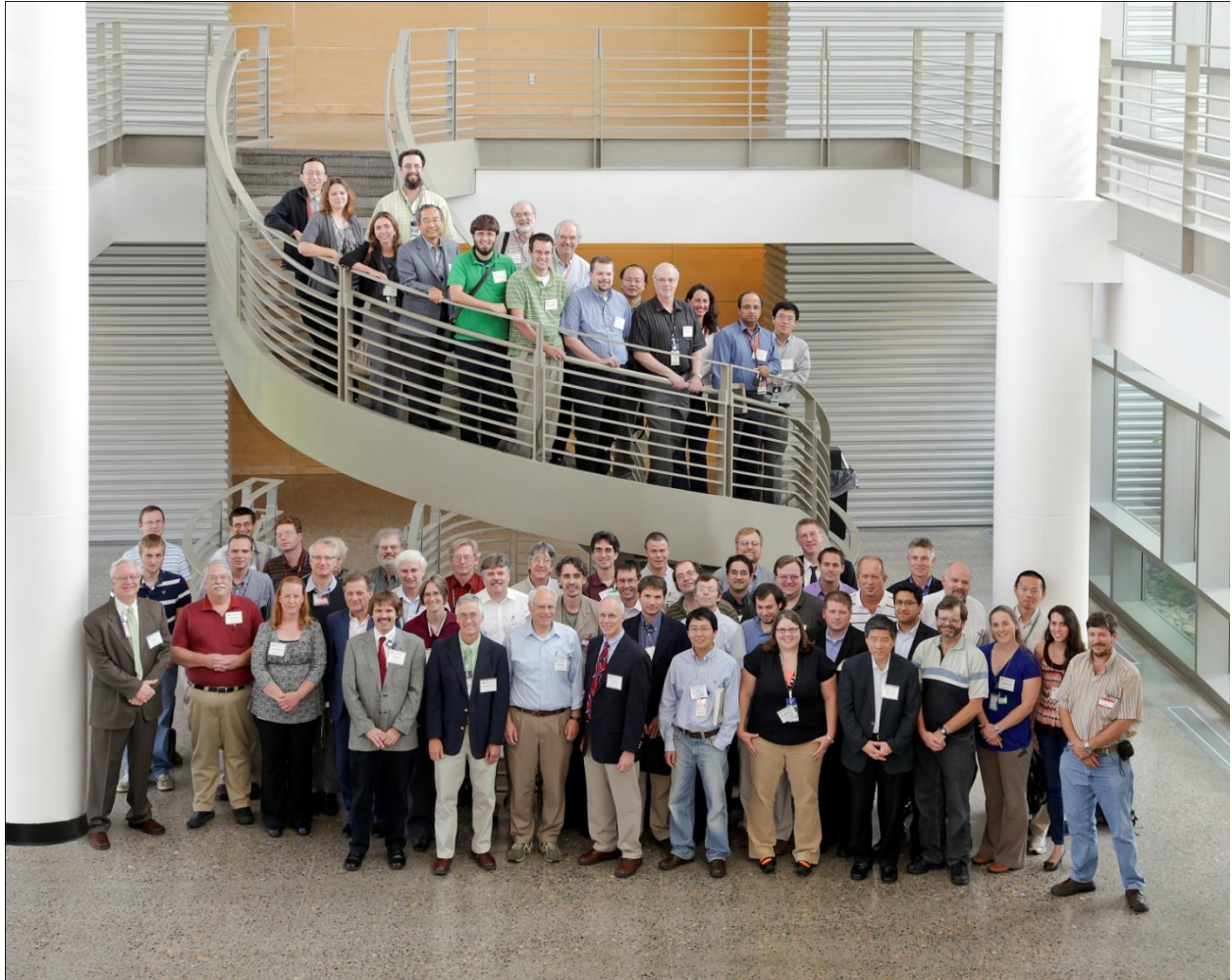
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## Appendix C Workshop photos



Workshop attendees



**Speakers (from left): Bruce Gates, Simon Bare (Discovery lecturer), Paul Langan, Jeronen van Bokhoven, Juergen Eckert, Thomas Proffen, David Sholl, Peter Albers , Peter Stair, and Timmy Ramirez-Cuesta.**





**Coffee break at the workshop**

## **Appendix D Organizing Committee**

### **Scientific Organizing Committee**

Steve Overbury, Chemical Sciences Division and CNMS, ORNL, Chair

Dean Myles, Neutron Scattering Sciences Division, ORNL

Peter Cummings, Vanderbilt University and ORNL

Viviane Schwartz, Center for Nanophase Materials Sciences, ORNL

Takeshi Egami, University of Tennessee and ORNL

Dave Wesolowski, Chemical Sciences Division and FIRST, ORNL

Phil Britt, Chemical Sciences Division, ORNL

Ken Herwig, Neutron Scattering Sciences Division, ORNL

Leighton Coates, Neutron Scattering Science Division, ORNL

Eugene Mamontov, Neutron Scattering Science Division, ORNL

Xiaoping Wang, Neutron Scattering Science Division ORNL

### **Local Organizing Committee**

Janice Allgood, ORNL

Al Ekkebus, ORNL

Toni Sawyer, ORNL

### **Contacts**

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