Neutrons for Catalysis: Structure

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Materials Science

Structure Breakout Goals

- Identify outstanding grand-challenge issues
- Identify relevant scattering-related information
- Identify relevant systems/materials/environments
- Identify any information needed to outline experiments
- Summarize for tomorrow's discussion

Structure "grand challenge" topics

- **Hydroxyl groups (-OH) on supports (location, ordering, defect passivation)**
- **Hydrogen and supported metals (surface, bulk, sub-surface, spillover to support, metal-support interface)**
- **Uniform metal clusters and nanoparticles in zeolites (ordering, metal-support interface, bimetallics)**
- **Zeolite synthesis (in-situ neutron diffraction and spectroscopy)**
- **Acid sites in zeolites (structure, location, adventitious water)**
- **Probe reactions (low T, high P, CO oxidation, WGSR)**

Relevant systems/materials/environments

Well-ordered, uniform catalytic materials probed by neutrons:

"structure underlies function"

- **Well-defined metal oxide powders, e.g., "nanocubes" (MgO, ceria, $SrTiO_3$)**
- **Highly ordered, high-surface area, catalytic materials (zeolites, MOF, mesoporous silicas)**
- **Organometallic complexes, molecular clusters and nanoparticles hosted in zeolites**
- **Molecular metal oxide clusters (silicas, heteropolyacids)**
- **1-2 nm Pt nanoparticles on alumina (narrow particle size distribution)**
- **Activated carbons and carbon-supported noble metals for liquid-phase hydrogenations (biofuels)**
- **Catalytic probe reactions: CO oxidation (low-T), water-gas-shift, organic hydrogenation**

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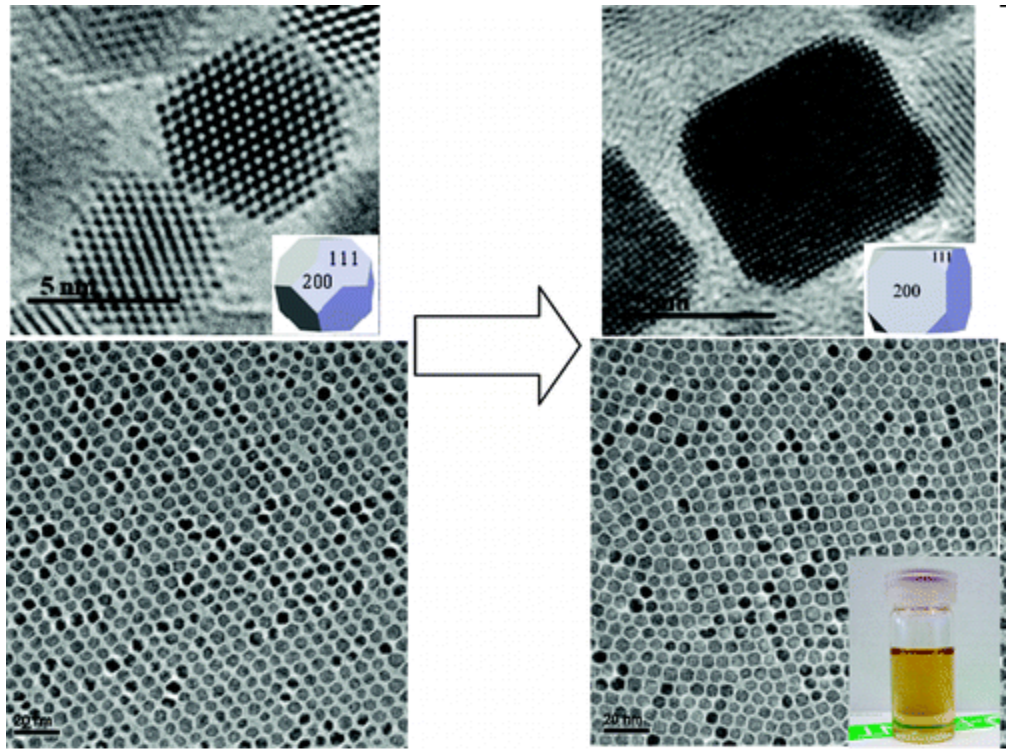
CeO_2 nanocubes and related polyhedra



F. Dang, et al., *Cryst. Growth Des.*, 2010, **DOI:** 10.1021/cg1008347

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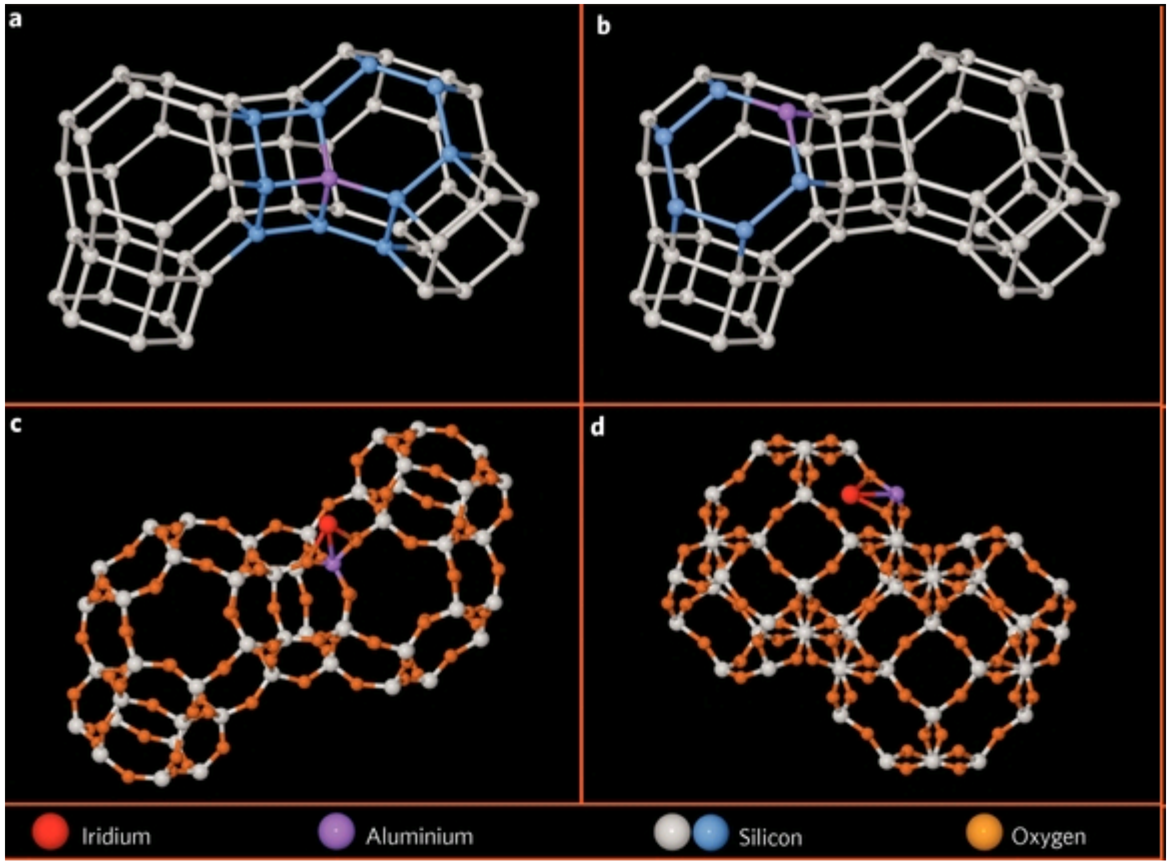
Anchoring of Ir complexes in Y zeolite



Gates and coworkers, Nature Nanomaterials, 2010

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Practical neutron science questions

- **Facilities for neutron powder diffraction (PDF), inelastic neutron scattering (INS), small angle neutron scattering (SANS): flux, resolution, availability (BASIS, CNCS, VISION)**
- **Complementary techniques (XAS, IR, Raman, XRD)**
- **Sample preparation and gas handling capabilities (T, P, H_2, CO, etc.)**
- **In situ cells for "high-pressure" (1-100 bar) gas-solid and liquid-solid catalytic reactions**
- **Low-temperature catalytic reactions**
- **Handling of irradiated samples (decay period, return to user or disposal)**

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Outstanding Grand-Challenge Issues

- **Identify outstanding grand-challenge issues**

Important to know the relative position of OH groups on surface of catalysts: attaching metals on an oxide surface and understanding the coordination of the metal to the surface; the questions are: how far apart are the metal centers; OH has been identifies as important factors to anchor metal species; how to characterize them?

Zeolites – crystalline support can be a good model as an ordered crystalline structure; that is a very similar question related to the OH groups location; it is not well understood how the synthesis proceeds; would be good to have in situ studies of the synthesis of zeolites; SANS studies available in this case; discussion regarding how many work is available regarding hydrothermal and zeolite synthesis using neutron techniques

OH groups on oxides and zeolites should be parallel (or better connected) to the issues of hydrogen on metal studies; Should use simpler samples to study OH groups on alumina or other oxides by studying such issues on zeolites.

Metal-support interface issue:

Need to study sub-surface species and how to relate with catalytic performance; limitations of INS due to low temperature measurements

Understanding bending versus streching models of OH

Should we recommend that experiments need to be done to compare with experiments performed using other techniques? Try to build from samples that are well structurally defined to create a foundation for further studies. (there are experiments done using hydrogen storage in zeolites) Characterization of acid sites on zeolites what happens between interactions of H_2O and Lewis acid sites and what we can learn from using neutron techniques.

What about very well defined oxide nano particles structures that are much better than amorphous support as a start up of such experiments. There is already a porposal to look at the interaction of water with well defined ceria nanoparticles.

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Outstanding Grand-Challenge Issues

- **Identify outstanding grand-challenge issues**
- **Can we understand the structure of bulk oxide nanomaterials; looking at the interface structure**

Can we get a PDF of a sample where a third of the surface of a zeolite is occupied by nanoparticles and where these particles are? is there a time scale for such experiments to observe intermediate species? First we need to understand the static structure and then further understand changes of this structure under certain catalytic conditions.

The challenge might have to be addressed from the synthesis issue, i.e., can we synthesize a designed catalyst for neutron measurements?

Question: what is the time scale of the synthesis? The process of cluster sysnthesis inside the zeolites has been characterized by X-ray tehcniques

Summary:

OH on surface to understand catalytic reaction: chanllenge is to design a material for such study using neutrons

Materials: zeolites, nanoparticles oxide

Surface-metal interaction

Questions about PDF technique: issue regarding core-shell particles; it is an average technique over the entire sample

What about bimetallic alloys analyzed by PDF? There are not mathematical tools to resolve these structures yet and it is needed known models (better , reference samples) to compare with the unknown sample

What about metals that activate on neutron beams, like cobalt? Some might need to characcterize the samples after neutron measurements

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Outstanding Grand-Challenge Issues

- **Identify outstanding grand-challenge issues**
- **What happens with the samples after the measurements? Is there any issue regarding sample damage during the experiments? Not really.**

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Relevant systems/materials/environments

- **Identify relevant systems/materials/environments**
- **Can we identify model samples that can highlight the structural effect of H and OH on the surface? Zeolite support with the cages filled with Ir clusters – this would be a problem maybe for neutron measurements since the neutron is highly absorbed by the element .**
- **Well defined ceria nanocubes or magnesia nanocubes**
- **How to identify defects on the surface; using the hydroxyl groups associated with the defect sites to address the grand challenge of identifying the defect sites.**
- **How to connect model single crystals; challenges of using model thin films is that such systems might not contain OH groups; how can one use low surface area materials such as model films or surfaces using neutrons**
- **What about larger particles and differentiate interface structure to bulk? Need to use nanosized metal particles on supports like alumina**
- **What about looking at the support by itself first, like zeolite to locate the acid sites and then introducing other elements/ Refractometer experiment to look at flat surfaces to investigate interface;**
- **What about environments? Reactors for neutron measurements during catalytic performance.**
- **Can we use a high pressure reactor ? Reactor up to 100 bar is already in place at SNS.**
- **Can we have a stirred reactor? There is not a reactor like this in place already but it can done if there is a special issue. Gases that can be used at SNS? Right now, there is already CO, CO2, H2 in place but other gases can be placed if passes RSS.**
- **What about the quality of the data at higher temperatures? Should we study reactions that take place at lower temperatures? From the structural point of view, we are not limited by temperature as we are limited in case of dynamic studies.**
- **What about looking at catalyst surface oxides under high pressure (100 bar) hydrogen atmosphere since there are already capabilities at SNS? Reactions like HDS are performed at these high pressures and catalysts used in these reactions would be of interest.**

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Relevant systems/materials/environments

- **Identify relevant systems/materials/environments**
- **SANS would be very good for studying micro porous material and studying liquid phase interface inside the pores.**

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Information needed to outline experiments

- **Identify any information needed to outline experiments**

Structure: Discussion Summary

- **Summarize for tomorrow's discussion**

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Relevant scattering-related information

- **Identify relevant scattering-related information**

From memory: Friday breakout on structure Maybe the original notes were lost.!

- When neutron scientist talk about high pressure reactors, the feasibility of HP experiments was discussed. It would be very nice to look at catalysts used for hydrotreating at high pressure H2 conditions. Even oredered materials like zeolites would be of interest. Supppose you want to put in H2 and increase pressure it would be very nice to see if sites would chage or what would happen. Then neutron scientist says problem is to distinguish H2 in gas phase from H2 on the surface. Would it help to use variable pressure?
- Hydroxyl groups, how to look at the hydroxyl on surface? The important factor is to find the atomic composition of the whole system. It is better to have more hydroxyls than anay other elements combined.
- These two points were the major ones described during the second breakout session.

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