

IV.I.17 Application of Neutron Scattering on Hydrogen Storage

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Recent Progress

The hydrogen activities described below represent a subset of a larger FWP (ERKCC01) identified above. That effort couples synthesis, advanced characterization (including neutron scattering) and computational and theoretical modeling. The primary objective is to discover and exploit controlled synthetic methods to produce, characterize and ultimately control novel inorganic nanometer-scale materials and to gain a fundamental understanding of how the spatial or temporal confinement of atomic or molecular species onto or within materials impact the physicochemical properties. These objectives are achieved using advanced characterization methods unique to the ORNL environment, including the world's brightest spallation neutron source (SNS), state-of-the-art, aberration-corrected, Z-contrast, scanning transmission electron microscopes with 1 Å or finer resolution, leadership-class computing capabilities as represented by petascale computers like Kraken and Jaguar, and the Center for Nanophase Materials Sciences (CNMS), combined with a team of expert personnel uniquely qualified to exploit these resources.

Hydrogen Interactions with Metal Oxide (MO) and Carbonaceous Material

We used inelastic neutron scattering (INS) spectroscopy techniques to obtain detailed information about H₂ interactions with a prototypical MO surface, i.e. MgO (100). INS techniques are *unrivaled* in sensitivity and precision for probing the rovibrational dynamics of condensed phase H₂ molecules [Mitchell, 2005]. They present several advantages over infrared spectroscopic and helium atom scattering methods for interrogating the dynamics of H₂ adsorbates: neutron scattering does not depend on the weak transition dipole moment induced in H₂ adsorbates by the underlying surface (i.e., no optical selection rules), neutrons can penetrate deeply through bulk matter to provide information about adsorbate dynamics in the multilayer adsorption regime, and, unlike infrared or helium atom scattering techniques, INS spectroscopy

can directly probe the para→ortho ($J=0 \rightarrow 1$) transition of H₂ adsorbates. INS studies of monolayer and multilayer H₂ films adsorbed on nearly defect-free MgO (100) surfaces were performed and interpreted with the aid of a reduced dimensionality quantum dynamical model for the H₂ adsorbates. Our studies show that, for this system, the $J=0 \rightarrow 1$ rotational transition previously observed in INS studies of both bulk H₂ and H₂ adsorbed on carbon-based materials is shifted to substantially lower energy due to interactions between the H₂ films and the MgO (100) surface. Our findings suggest that these interactions substantially hinder the adsorbates' end-over-end rotational motion enough that the first-layer H₂ molecules acquire partial two-dimensional (2D) character. These studies are made possible by the size-selectable, chemically pure, MgO nanocubes produced by our patented process (Kunmann-Larese U.S. Patent #6.179.897, 2001) that involves decomposition of an intermediate Mg carbide phase. Detailed high-resolution thermodynamic studies (Frazier, PhD thesis UTK 2008) have provided a roadmap for exploring the phase diagram. At submonolayer coverage H₂ forms a commensurate c(2x2) phase. An increase in the monolayer surface density results in a devil's staircase set of transitions involving uniaxially compressed p(2x4) and p(2x6) solids. At monolayer completion, a hexagonal solid form that is 25% more dense than the closed-packed phase of bulk H₂ at the same temperatures (see Figure 1). Our INS results indicate, and our computational studies substantiate, that the INS feature observed at 11.3 meV using H₂ and 8.0 meV using HD, is associated with hindered, quasipolar rotational motion of molecular hydrogen adsorbed atop Mg²⁺ cations on the MgO (100) surface (see Figure 2). For reference, we include in Figure 2 the INS response of a commensurate ($\sqrt{3} \times \sqrt{3}$ R 30°) monolayer of H₂ on the basal plane of graphite, which exhibits the same unhindered rotational motion as the H₂ bulk solid or gas phase (i.e. the para→ortho transition at 14.7meV). The melting temperature of the compressed monolayer solid appears to be about 25-30K. The combination of INS, thermodynamics, diffraction and theory has played a valuable role in understanding this fascinating system. These efforts are aimed at obtaining a quantitative model for the H₂-MgO interaction that can be used to understand H₂ adsorbate dynamics in both monolayer and multilayer films.

In addition to the interaction of hydrogen with pure MOs we have expanded our investigation to include the interaction of molecular hydrogen with nm-sized metal clusters decorating the MOs. These studies are aimed at developing a better understanding of H₂ interactions with these dispersed metal clusters and how the interaction of H₂ with the metal cluster is modified

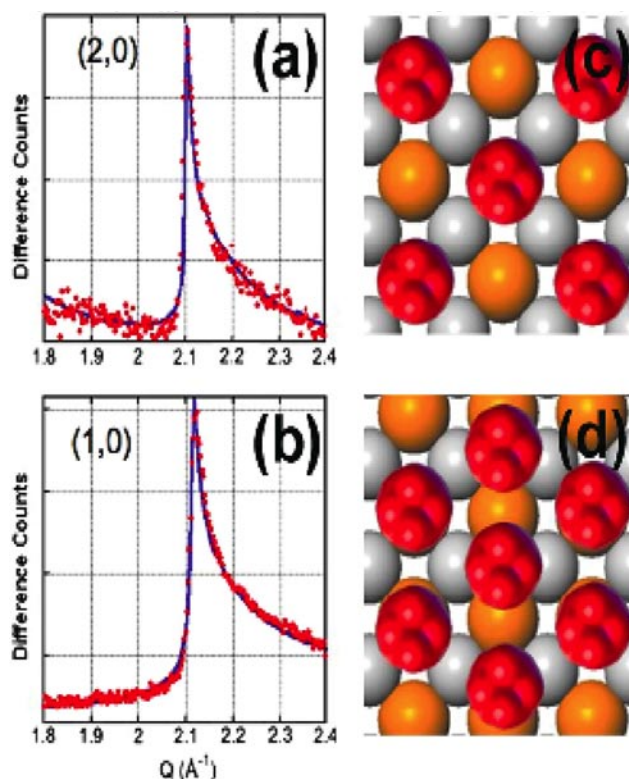


FIGURE 1. Neutron diffraction profiles (a) and (b) and schematics of solid structures (c) and (d) for $c(2 \times 2)$ submonolayer (c) and complete monolayer (d).

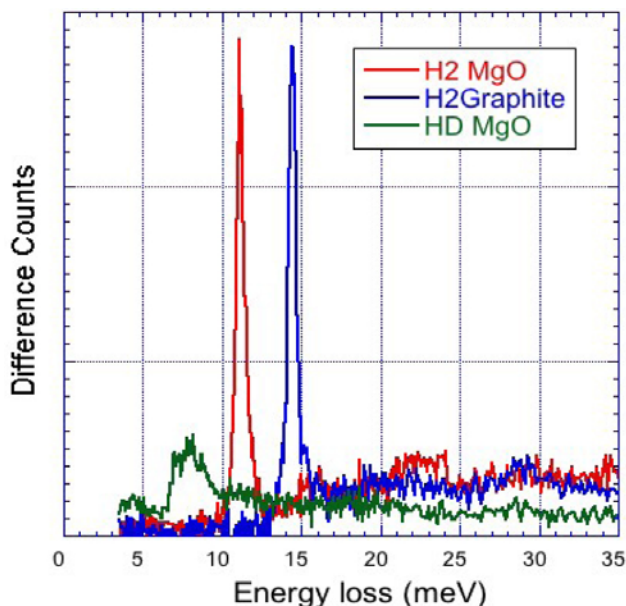


FIGURE 2. INS spectra collected using TOSCA spectrometer at ISIS spallation source. The individual spectra are the INS response from monolayer films.

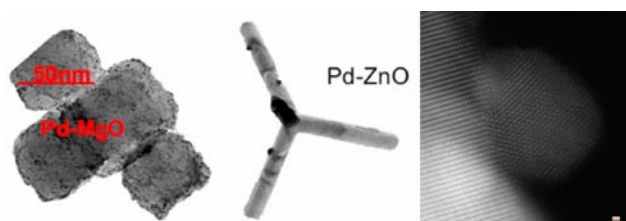


FIGURE 3. STEM micrographs of Pd decorated (left) MgO nanocubes and (center) ZnO tetrapod and (right) ZnO/Pd interface. The Pd nm particle is at the right of the figure.

by the MO support. We want to determine what role the MO plays in stabilizing the nm scale metal cluster and how the physicochemical properties of the metal (and/or the support) are changed. MOs are routinely used for supports for catalysts and we are interested to see how the crystal and electronic structure of the metal cluster is affected by the adjacent MO interface. Our latest investigations focused on synthesis and characterization of Pd decorated ZnO and MgO nanoparticles. Figure 3 shows representative electron micrographs of the Pd decorated nanomaterials. It is especially interesting to note the high-resolution image of the Pd-ZnO interface where the interface is easily resolved. Preliminary analysis of photoemission measurements for the nm Pd clusters on the ZnO indicate that the Pd3d core level spectrum appear to be unshifted from bulk Pd metal, however, a more careful examination of the results are underway. Furthermore, preliminary INS measurements of H_2 adsorption on the Pd decorated ZnO suggest that all of the H_2 molecules adsorb *molecularly* (i.e. below saturation) at the Pd sites and that the bound length increases by $\sim 6\%$ based on the shift of the para \rightarrow ortho transition energy to lower values.

Modeling of H_2 with nm-Scale Metal Decorated Metal Oxide Particles

The adsorption properties of molecular H_2 with Pd and ZnO and Pd decorated ZnO are currently being investigated using *ab initio* calculations with the Siesta implementation of density functional theory (DFT) within the local spin density approximation (LSDA) for the exchange and correlation functional.

Modeling of pristine ZnO and Pd surfaces confirms that upon exposure to gaseous H_2 , the molecule dissociates and a hydride layer is formed. For the Pd nanoparticle(cluster), the preferred adsorption site is in the center of the triangles formed by the close-packed Pd atoms, which are in the face centered cubic (FCC) configuration. For the ZnO, each of the hydrogen atoms is attached to either a Zn or an O atom (see Figure 4).

The DFT modeling of the adsorption of H_2 in Pd decorated ZnO structures is under development. Currently, our studies focus on understanding the

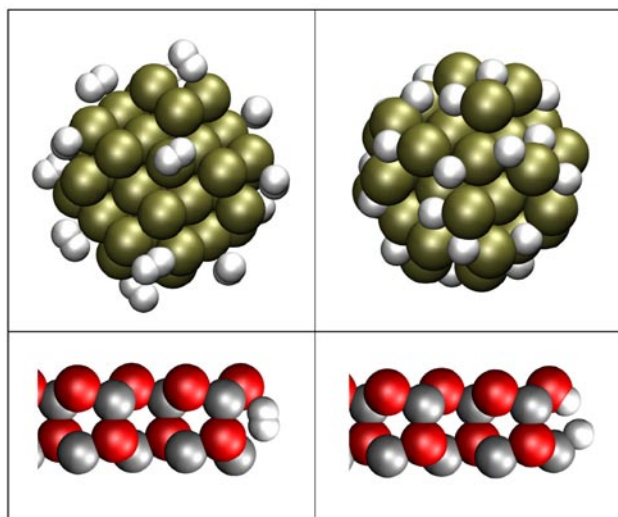


FIGURE 4. Evolution of the absorption of hydrogen in a palladium nanoparticle (a,b) and a zinc oxide surface (c,d) . (a,c) are the initial states, and (b,d) final states.

interaction of the Pd nanoparticle with the ZnO host before we address the H₂ adsorption modeling thus mimicking the experimental procedure. Hence, the interactions of two different surfaces of the Pd cluster with three surfaces of the ZnO were investigated, produces six different configurations to be studied.

Consideration of these six configurations, coupled with an ~1 nm Pd cluster size and the minimum thickness of the ZnO slab to reproduce surface effects, have resulted in a highly demanding computational effort, where each system is formed by about 650 atoms.

To address this computational limitation, we have also modeled a Pd cluster deposited on of a ZnO nanorod to explore the interaction of these systems in a smaller system. In this case, the computational speed has improved; we observe that the first four layers of atoms rearrange, some atoms that comprise the first ZnO layer “attach” to the side of the Pd nanoparticle (i.e. the particle is ‘wet’ by the host), indicating a high affinity for the absorption of the Pd nanoparticle (see Figure 5). We note the general similarity to high-resolution micrograph in Figure 3.

Currently our modeling is still incomplete, computationally the system is not yet fully relaxed. The H₂ adsorption studies will be performed when the Pd/ZnO system is relaxed. However, semi empirical calculations of the combined system show that charge transfer effects cause hydrogen to stretch by about 15% and adsorb in the surface of the Pd cluster, in general accord with the experimental results.

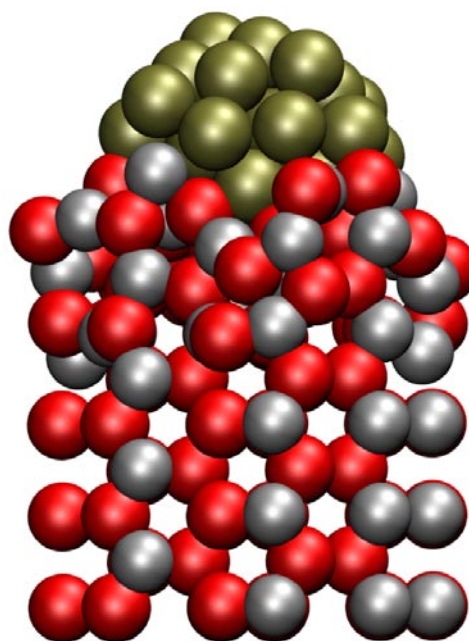


FIGURE 5. Nanoparticle deposited upon a ZnO nanorod. The wetting of the Pd particle is observed in the displacement of the Zn and O atoms in the vicinity.

Published Papers/Thesis citing BES support

1. Larese, J.Z.; Arnold T.; Barbour A.; Frazier L. Neutron Investigations of Rotational Motions in Monolayer and Multilayer Films at the Interface of MgO and Graphite Surfaces, *Langmuir* **25**, 4078 (2009).
2. Larese, J.Z.; Arnold, T.; Frazier, L.; Hinde, R.J. and Ramirez-Cuesta, A. Direct Observation of H-2 Binding to a Metal Oxide Surface *Phys. Rev Lett.* **101**, 165302 (2008).
3. Frazier, L.R. “Molecular Hydrogen Adsorbed on MgO (100) Surfaces: A Thermodynamic Study”, PhD Thesis, December 2008, University of Tennessee, Knoxville, Chemistry Dept .(J.Z. Larese Advisor).
4. Larese, J.Z.; Frazier, L.; Adams, M.A.; Arnold, T.; Hinde, R.J.; Ramirez-Cuesta, A. Direct Observation of Molecular Hydrogen Binding to Magnesium Oxide (100) Surfaces, *Physica B*, **385**, 144 (2006).

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