
Neutron scattering aided studies of the design, synthesis and thermodynamics of molecular hydrogen adsorption materials

J. Z. Larese^{†*}, Lillian Frazier^{*}, Thomas Arnold[†], Michael Farinelli^{*}, Michael Hu[†], David Beach[†], A.J. Ramirez-Cuesta⁺, and R.J. Hinde^{*}

[†]Oak Ridge National Laboratory,
Oak Ridge, TN 37831

^{*}Chemistry Dept., University of Tennessee, Knoxville, TN, 37996

⁺ISIS Spallation Neutron Facility, Rutherford-Appleton Laboratory, Chilton,
England

Program Scope

Our basic research activities relevant to the DOE hydrogen program are part of our larger program in Materials Chemistry. This abstract concentrates on how our combined neutron scattering, thermodynamic, synthetic, and computational investigations of the structure and dynamics of molecular adsorption and liquid entrainment impact the development of new knowledge and materials relevant to the hydrogen initiative. Our program focuses on the development of accurate potential energy surfaces to describe the interaction of molecular hydrogen with solid surfaces and within porous media to ultimately achieve predictive powers to tailor-make new materials.

During the early phases of our investigations, several key milestones have been achieved:

- The application of novel synthetic methods to produce large quantities of morphology controlled pure and doped nm scale metal oxide (MgO, ZnO). In addition, we have produced size adjustable, nm scale, metal oxide and amorphous carbon materials with ordered, uniform arrays of cylindrical channels.
- The use of precise volumetric adsorption isotherm methods to effectively identify the wetting properties and heats of adsorption in gas surface reactions, and to identify thermodynamic regions of interest where neutron scattering studies can be performed on these new materials.
- Identification of the density-structure-dynamics relationship of molecular hydrogen adsorption on MgO(100) surfaces and entrainment within cylindrical channels introduced into porous carbon and anodically anodized metal oxides materials.
- Development of computational methods to model the adsorption properties and potential energy surfaces.

Recent Progress

(a) *Investigations of the effect of confinement on the structure, dynamics and adsorption properties of molecular hydrogen and hydrogen bearing small molecules.*

Adsorption Isotherms

Volumetric adsorption isotherm techniques are a well-established, widely employed and accurate method to gauge the adsorption properties of porous and high surface-to-volume ratio materials. In addition to defining the gas capacity, isotherms are used to determine

the heat of adsorption, the isothermal compressibility, and to delineate phase and wetting transitions. We developed a computer-automated instrument to perform adsorption isotherms volumetrically. This device is used at various neutron facilities for combined *in-situ* thermodynamic and neutron diffraction and inelastic scattering experiments. In Figure 1(a) we illustrate the layering behavior of H₂ on the MgO(100) surface. The step-wise increase in the amount adsorbed clearly shows the formation of at least seven discrete H₂ layers on the MgO(100) surface. By collecting adsorption data at different temperatures we can determine the heats of adsorption that are used to aid and constrain the theoretical models that are developed to describe the interaction of hydrogen with our materials. Naturally, not all materials show the layer-by-layer condensation of molecular hydrogen. In Figure 2 we show several adsorption isotherms performed using D₂ on aligned arrays of cylindrical channels in an amorphous carbon raft. As noted above, these measurements can be used to calculate a heat of adsorption.

Neutron Diffraction

Molecular systems confined to planar surfaces or entrained in well-defined channels or pores exhibit distinct diffraction lineshapes that can be used to identify details about the local structure and morphology of the adsorbed phase. Molecular films that grow on surfaces like an ideal 2D solid exhibit characteristic lineshapes that look like a kerf of a sawblade. Such behavior is recorded in our studies of D₂ adsorbed on MgO(100) surfaces in Fig. 3. Here we illustrate the variation of the structure of the solids formed in the layer closest to the surface both as a function of density and temperature.

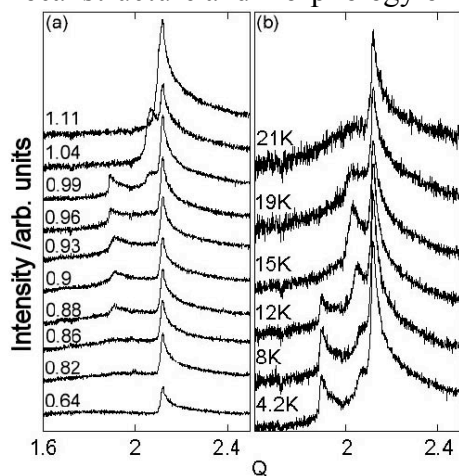


Fig. 3 Neutron diffraction difference scans as a function of (a) coverage (mnl) and (b) temperature (0.9 mnl)

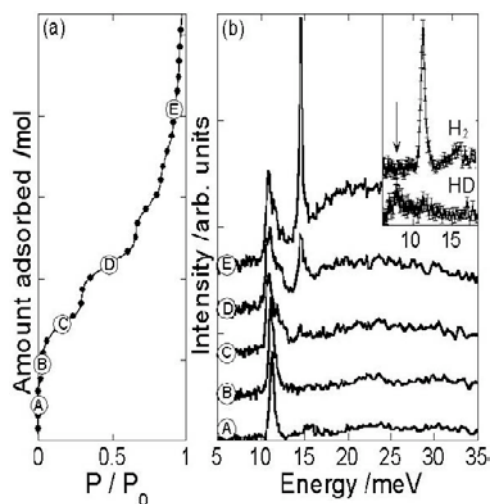


Figure 1. H₂ on MgO (a) 12K isotherm (b) INS spectra recorded at coverages noted in (a).

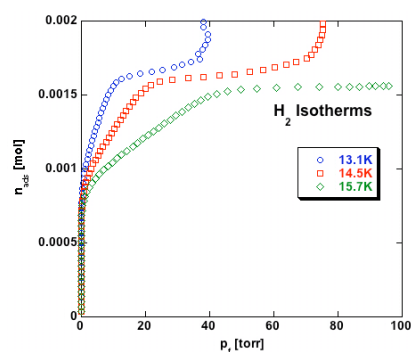


Fig. 2. Adsorption isotherms of H₂ on carbon pore materials.

At low coverages the H₂ forms a c(2x2) solid, commensurate with the MgO(100). Our measurements show that by increasing the surface density results in a series of commensurate structures that are of the form (2x2n) where n=2,3,4 this formation of sequential commensurate solid structures is referred to as a devils staircase. Near monolayer completion a

close packed hexagonal phase forms. These diffraction data are being used to constrain and refine the hydrogen MgO interaction potential.

Inelastic Neutron Scattering (INS)

Inelastic neutron scattering is unrivalled in its sensitivity to the dynamical motion of hydrogen bearing molecules. Fig. 1 (b) illustrates coverage dependence of the INS spectra recorded using a time of flight spectrometer TOSCA at the ISIS spallation neutron facility at $\sim 10\text{K}$ at film thicknesses indicated on the isotherm. The energy transfer range where the H_2 free rotor ($J = 0 \rightarrow 1$) transition is observed in the bulk solid (14.7 meV) is highlighted. For surface coverage, $\theta \leq 0.8$ (monolayers) this para-ortho transition occurs at 11.25 meV with an energy profile very close to the instrument resolution function. To our knowledge, such a clean shift in the position of this transition has not previously been observed on any material. To verify that this transition is related to the rotational motion of the molecule we performed an INS measurement at nearly the same coverage with an HD film (see inset to Fig. 1(b)). Although the scattering density of HD is significantly lower than for H_2 we are still able to obtain a small but statistically significant signal at ~ 7.9 meV. When H_2 molecules adsorb non-dissociatively on a surface, H_2 -surface interactions mix together the roto-vibrational quantum states of gas-phase H_2 molecules, much like applying an external field to an atom leads to orbital hybridization by mixing together field-free atomic eigenstates. As a result, the energy levels of the adsorbed H_2 molecule differ from those of gas-phase H_2 molecules. Using an empirical H_2 -MgO adsorption potential energy function to compute the quantum mechanical rotational states of isolated H_2 molecules physisorbed on the $\text{MgO}(100)$ surface we find that in the $c(2 \times 2)$ phase (i.e. $\theta \leq 0.8$) the molecules adsorb above Mg^{2+} ions on the $\text{MgO}(100)$ surface and that rotational motion is hindered by the attractive influence of the substrate such that it is more planar than spherical in nature. The broadening of the high energy side of the spectrum signals the appearance of molecules not located above the Mg ions while at $\theta > \sim 3$ a signal appears from molecules that see a rotational potential similar to that in the bulk solid.

(b) Development of synthetic methods to tune/control the composition, morphology and size distribution of novel metal oxides with unique physical and chemical properties.

Metal oxides are widely used in catalysis, gas separation, sensor technology, micro and optoelectronics, cosmetics and medicine. The production of nanometer scale, well-

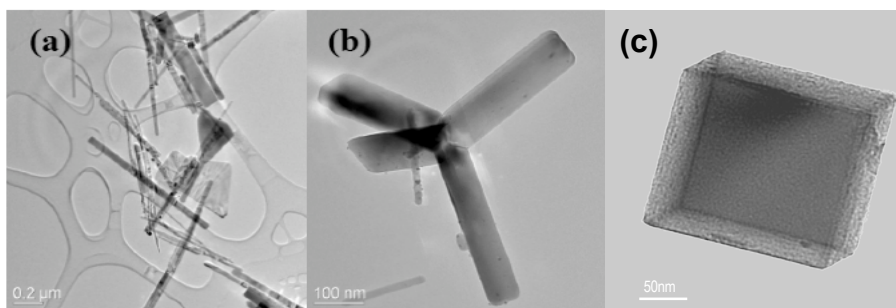


Fig. 4 Sample electron micrographs of ZnO (a) rods and plates and (b) tetrapod and (c) a Typical MgO nanocube.

characterized, pure and doped metal oxides with high surface to volume ratio and thus a large capacity for hydrogen storage and or rapid gas cycling

remains a technological but realistic challenge. Larese and Kunmann [US. Patent # 6,179,897] have recently developed a unique method for the production of size, morphology and compositionally controllable metal oxide (MO) materials with the formulation $M_{(1-x)}R_xO$, where M/R include Mg, Zn, Ni, Li, Cr, Cu, and Sn. To date, our efforts have focused on producing MgO and ZnO compounds (Figure 4). We have recently investigated the synthesis and study (see Figure 1 for adsorption isotherm) of amorphous carbon materials that have an aligned array of hexagonally ordered cylindrical channels.

Figure 5 is a typical electron micrograph of the morphology of one of the of these porous carbon materials. The pore diameter is ~ 2.5 nm and the typical thickness of the carbon wafer is about 1 μ m.

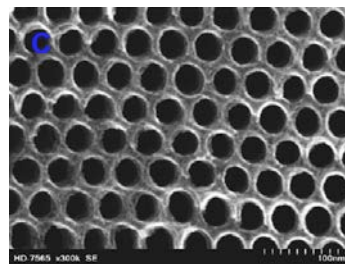


Fig. 5 Electron micrograph of amorphous carbon materials with a hexagonally ordered network of aligned cylindrical Channels.

Recent relevant publications

Arnold, T., S. Chanaa, S. M. Clarke, R. E. Cook, J. Z. Larese. *The structure of an n-butane monolayer adsorbed on Magnesium Oxide (100)*. To be published Phys. Rev. B. 2006.

Drummond, M. L., B. G. Sumpter, W. A. Shelton, and J. Z. Larese. *Density functional investigation of the adsorption of a methane monolayer on an MgO(100) surfaces*. To be published Phys Rev B 2006.

Larese, J. Z., L. Frazier, M. A. Adams, T. Arnold, R. J. Hinde and A. Ramirez-Cuesta. *Direct observation of molecular hydrogen binding to Magnesium Oxide (100) surfaces*. To be published Physica B 2006.

Arnold, T., R. E. Cook, S. Chanaa, S. M. Clarke, M. Farinelli, P. Yaron, J. Z. Larese. *Neutron scattering and thermodynamic investigations of thin films of n-alkanes adsorbed on MgO(100) surfaces*. To be published Physica B 2006.

J. Z. Larese, R. Hinde, L. Frazier, T. Arnold, M. Adams, M. Telling and A. Ramirez-Cuesta, *Direct Observation of Molecular Hydrogen Binding to Metal Oxide Surfaces*, ISIS 2005 Scientific Highlights, ISIS Annual Report, Rutherford Appleton Laboratory, www.isis.rl.ac.uk.

Arnold, T., R. E. Cook, J. Z. Larese. *Thermodynamic Investigation of Thin Films of Ethane Adsorbed on Magnesium Oxide*. J. Phys. Chem. B. 109 (2005) 8799.

Pearce J. V., S. O. Diallo, H. R. Glyde, R. T. Azuah, T. Arnold and J. Z. Larese. *Enhanced Bose-Einstein condensation and kinetic energy of liquid ^4He near a free surface*. J Phys.: Condens. Matter. 16 (2004) 4391.