From Fundamental Understanding to Predicting New Nanomaterials for High-Capacity Hydrogen Storage

Jason Simmons, Wei Zhou, Taner Yildirim, John E. Fischer

University of Pennsylvania and NIST Center for Neutron Research

I. H_2-Storage Materials: Current Impasse

Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of hydrogen and fuel cell technologies. Currently,

No material is known to be practical for H_2 Storage !

Physisorption materials
→ relatively low capacity
→ very low desorption temperature

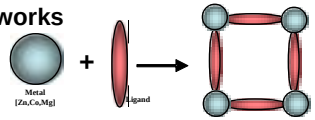
Chemical hydride / metal hydride
→slow kinetics
→ poor reversibility
→high dehydrogenation temperature

Combined theoretical and experimental investigations will enable the development of novel concepts and approaches to fill this gap

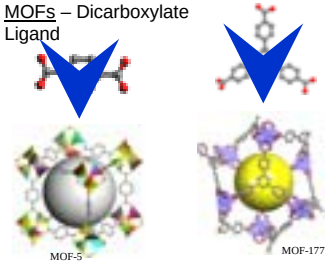
II. Promising Hybrid Materials

Improved nanoporous frameworks

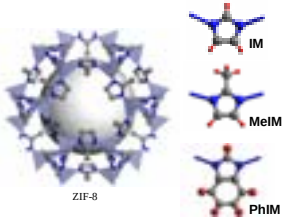
General synthetic scheme for organic-inorganic frameworks:



MOFs – Dicarboxylate Ligand

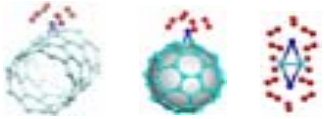


ZIFs – Imidazolate Ligand



Enhanced binding through Kubas interaction

Transition metal – Hydrogen interaction with intermediate binding energy



Calculations for carbon nanostructures

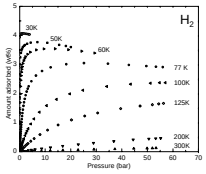
- Also focus on experimentally doping other promising host lattices
- High temperature stability of ZIFs permits chemical vapor deposition of transitions metals

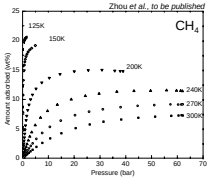
Supported by DOE-BES DE-FG02-98ER45701 and EERE DE-FC36-04GO14280

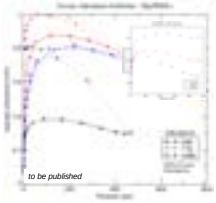
III. Direct Adsorption Measurements

Home built Sieverts apparatus for variable temperature and pressure adsorption studies

ZIF-8
- Initial heat of adsorption of H_2: ~4.5 KJ/mol
- Maximal H_2 adsorption capacity: ~4 wt%
- Similar heat of adsorption though lower capacity than MOF-5

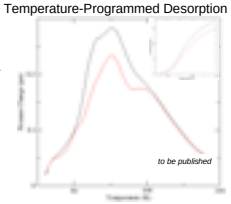






New Mg(PhIM)$_2$ framework:
- Significant absorption hysteresis at low temperature
- Strong kinetic effects – higher adsorption for longer loading times (left, inset)
- Developing low temperature TPD capabilities (right) to compare to total energy calculations

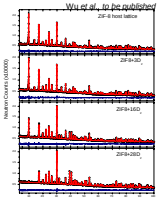
Temperature-Programmed Desorption



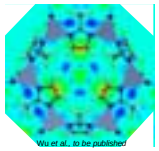
IV. Neutron Scattering Capabilities

Hydrogen has a large neutron scattering cross section, making neutrons a powerful probe of hydrogen structure and dynamics

Neutron diffraction for determining adsorption sites
- Refinement of diffraction pattern gives detailed structural information
- Difference Fourier technique shows real space positions of adsorbates

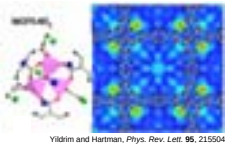


ZIF-8



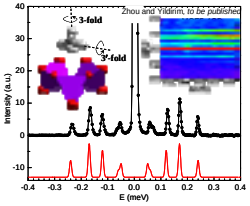
Initial adsorption on ligand

In **MOF-5**, initial adsorption is at metal center



Yildirim and Hartman, *Phys. Rev. Lett.* **95**, 215504

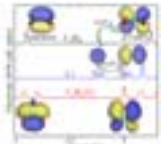
Inelastic Neutron Scattering
- Determine lattice dynamics and structural stability of host lattice
- Probe potential energy surface experienced by adsorbates
- Yields phonon energies as well as barriers to vibrational and rotational transitions
- Measure diffusion of adsorbates in the lattice



V. First Principles Calculations

Density Functional Theory
- Determine stability of adsorption sites; augments neutron diffraction studies
- Detailed picture of hydrogen adsorption in novel structures

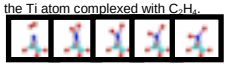
A $C_2H_4Ti_2$ complex with 10 molecularly bound H_2. The bonding orbitals for the top and side H_2 are shown. Note that the hydrogen σ^*-antibonding orbitals are hybridized with Ti-d orbitals, suggesting a Kubas interaction for the H_2-Ti bonding.

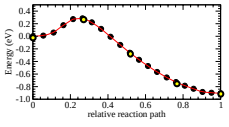


Electronic DOS of C_2H_4, Li atom, and C_2H_4+Li complex. The hybridization of the Li-2*p* state and the LUMO of C_2H_4 is apparent.

- Calculation of reaction barriers

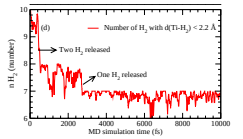
The minimum energy path for the dissociation of an H_2 molecule over the Ti atom complexed with C_2H_4.





Molecular Dynamics
- Study stability and desorption of H_2

Stability plot for the $C_2H_4(Ti+5H_2)_2$ sandwich complex at 500K showing the successive desorption of H_2 molecules in the course of the simulation.



Durgun *et al., Phys. Rev. Lett.* **96**, 226102 and Zhou *et al., cond-mat*, 0701569

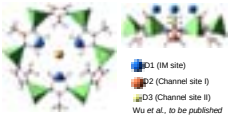
VI. Looking Forward

- Use a combination of experimental and theoretical studies to understand the detailed guest-host interactions in novel storage materials

Structure

Synthesis
Doping
Adsorption

Neutron diffraction
Neutron scattering
DFT/MD



- Armed with this, develop advanced guest-host materials that can meet the DOE hydrogen storage challenge