IV.C.5 A Joint Theory and Experimental Project in the High-Throughput Synthesis and Testing of Porous COF and ZIF Materials for On-Board Vehicular Hydrogen Storage

Omar M. Yaghi
Department of Chemistry and Biochemistry
Center of Reticular Chemistry at
California NanoSystems Institute
University of California, Los Angeles
607 Charles E. Young Drive East
Los Angeles, CA 90095
Phone: (310) 206-0398; Fax: (310) 206-5891
E-mail: yaghi@chem.ucla.edu

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

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Objectives

- High-throughput computational screening to identify new materials for favorable H_2 uptake.
- High-throughput preparation/characterization of doped materials predicted for high uptake.
- High-throughput screening to testing a diverse set of compositions and structures.
- Develop chemistry and perform computational testing of Li/Na/K doping effects on H_2 uptake.
- Predict and determine heat evolved upon reversible uptake and release.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rates
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of conducting fundamental studies of covalent organic frameworks (COFs) and zeolitic imidazolate frameworks (ZIFs). Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage system targets:

- Volumetric density: 40 g L^{-1}
- Gravimetric density: 5.5 wt%

Approach

Storage of hydrogen in porous materials is a promising approach to achieve the DOE system requirements for use of hydrogen as a transportation fuel. Since the first report of successful hydrogen storage in metal-organic frameworks (MOFs), we and others have succeeded in incrementally increasing the gravimetric and volumetric capacities to reach the highest hydrogen uptake capacity, albeit at 77 K. However, for on-board vehicular hydrogen storage it is necessary to improve the adsorption enthalpy of porous materials to achieve significant capacities at room temperature.

In this project period, we will implement metal impregnation in new classes of porous materials, COFs and ZIFs, to achieve room temperature hydrogen storage. COFs and ZIFs have the designable qualities of MOFs, but with features previously unattained in MOFs: (i) COFs are the least dense (0.17 g cm^{-3}) crystalline materials known, and they are replete with six-membered carbon rings ideally suited for impregnation with electropositive dopants such as Li, Na and K, and (ii) ZIFs are replete with metal ions linked with aromatic imidazolates whose electronic character can be tuned to enhance binding of hydrogen.

We plan to implement high-throughput synthesis protocols to discover metal impregnated COFs and ZIFs, and the resulting materials will be evaluated by high-throughput characterization techniques. More importantly, we combine theory/simulation with material synthesis and characterization, which will allow our team to rapidly scan promising classes of materials.

Accomplishments

- For high-throughput COF discovery, a stainless-steel reaction plate with 24 wells was designed and prepared. Conventional COFs were successfully reproduced using this new system.
- Synthesis of new ZIFs for metal impregnation. High-pressure H_2 isotherms of ZIF-68 ($Zn(C_7H_5N_2)(NO_2\text{-}C_3H_2N_2)$, 2.7 wt% at 77 K and 35 bar) and ZIF-76 ($Zn(C_3H_3N_2)(Cl\text{-}C_7H_4N_2)$, 2.2 wt% at 77 K and 46 bar) were also recorded.
- Total H_2 uptake in Li-impregnated COF-102 ($C_{25}H_{24}B_4O_8/8Li$) at 298 K has been calculated (8.2 wt% (42 g L^{-1}) at 100 bar), which shows optimal Q_{st} values (31 - 22 kJ mol^{-1}). The amount of H_2 delivered for Li/COF-102 is 4.0 wt% (20 g L^{-1}) when the pressure ranges from 5 to 100 bar.
- Began modeling study of five new 3-dimensional COFs and predicted their H_2 uptake capacity at 77 K.

Future Directions

- Develop new force fields for modeling adsorption properties of ZIFs and COFs. Test models using reported adsorption data for a range of known ZIFs and COFs.
- Experimentally explore metal impregnation conditions in existing ZIFs and COFs, and characterize metal density in the frameworks. Compare with predictions from theory.
- Investigate pressure and temperature dependence of H_2 uptake in impregnated existing ZIFs and COFs over the parameter range specified n revised DOE 2015 guidelines (5.5 wt% and 40 g L^{-1} up to 100 bar, -30/50°C). Compare with predictions from theory.
- Discover new ZIF and COF materials utilizing high-throughput methods and explore hydrogen uptake properties of ZIFs and COFs in the same parameter range.