IV.C.6 Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

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Contract Number: DE-FG36-08GO18139

Project Start Date: January 1, 2009
Project End Date: December 30, 2012

Fiscal Year (FY) 2011 Objectives

- Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H_2 storage at 300 K-400 K and moderate pressures.
- Optimize volumetric analyzer to increase precision and accuracy at high-pressure.
- Improve better dispersion of nano-metal catalysts, and examine uptake of MMOFs mixed with catalysts. Vary catalyst mixing technique to ensure optimal interfacial contact for spillover.
- Demonstrate spectroscopic evidence for spilled over atomic hydrogen in a Pt/carbon system, to help resolve potential confusion regarding physisorption versus chemisorption in spillover materials.

Technical Barriers

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

(A) System Weight and Volume
(D) Durability: Min/max temperature/maximum pressure
(E) Charging/Discharging Rates
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets

TABLE 1. System Gravimetric Capacity 2010/2015 Target (0.045/0.055) of Hydrogen Uptake via Spillover at 298 K

Sample	Pressure (bar)	Hydrogen in excess of He (kg H_2/kg)
PtC+IRMOF-8 (8 replicates; changes in mixing)	70-85	0.0028-0.0078
PtC+IRMOF-8 with bridging	70	0.0025-0.0030
Pt/M (Maxsorb Activated Carbon)	70	0.0079/0.0091[a]
Pt/MAr (950°C Ar anneal prior to doping)	70	0.0097[a]
Pt/MV (1,000 K vacuum anneal)	70	0.0101[a]
Pt/MKOH (KOH oxidation before doping)	70	0.0085[a]
Pt/MHNO$_3$ (oxidized in 70% HNO$_3$)	70	0.0093[a]
PtC/MMOF=O[c]	72	0.0017
PtC/MMOF-OH[c]	71	0.0069
Pt/AC-INER[b]	1	0.012

[a] Includes He adsorption correction for compatibility with literature.
[b] Provided by C.S. Tsao (INER, Institute of Nuclear Energy Research, Taiwan). Uptake is gravimetric. This sample used for subsequent in situ spectroscopy tests.
IRMOF – isoreticular metal organic framework

FY 2011 Accomplishments

- Improved accuracy of differential volumetric equipment 12-fold.
- Validated system against National Renewable Energy Laboratory blind sample.
- Explored mixing conditions on reproducibility of spillover of PtC/IRMOF. Demonstrated catalyst-MMOF contact needs improvement.
- Began new catalyst-MMOF mixing techniques.
- Demonstrated 22% increase in Maxsorb activated carbon after incorporating well-dispersed Pt catalyst.
- Demonstrated 1.2 wt% uptake on Pt/AC-INER at 1 bar and 298 K (supplied from collaborator INER, Taiwan).
- Synthesized new MMOFs with variations in surface chemistry for spillover studies.
- Developed MMOFs of high thermal and water stability by eliminating M-N bonds.

- Explored conditions to produce nanocrystals of MMOF samples for more efficient and uniform mixing with Pt/carbon catalyst.
- Raman in situ spectroscopy for the evidence of spilled over atomic hydrogen in Pt/carbon system and clarification of physisorption vs. chemisorption issue.
- Identified hydrogenation site for PtC/CuBTC via Fourier transform infrared and Raman spectroscopy.

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Introduction

The term hydrogen spillover has been used to describe a synergistic effect between high-surface area adsorbents and associated catalysts. The associated catalyst may act to dissociate molecular H_2 into atomic H species. The atomic H is then free to migrate to surface sites on the high-surface area support; the net surface H concentration is a function of the relative rates of surface migration versus desorption from the surface. This process occurs at moderate temperature (i.e. 300 K) and generally leads to a much higher uptake than expected for the metal catalyst or high-surface area adsorbent alone. Spillover materials using MMOFs have been reported to have high uptake at ambient temperature: bridged ('br') PtC/IRMOF8 achieved 4 wt% excess adsorption at 100 bar and 298 K [1]. Independent groups have demonstrated up to 4.2 wt% at 6.9 MPa after extended equilibration for brPt/C/IRMOF-8 [2]. Subsequent reports on spillover materials at room temperature have varied from less than physisorption to almost 9 wt%, demonstrating difficulties in reproducibility and invoking controversy. These uptakes approach DOE goals; however, as the process is highly dependent upon synthesis, measurement, and catalytic particle size [3,4], the process remains poorly understood. It is anticipated that optimization of the MMOF structure, surface chemistry, and porosity will further increase uptake via spillover. Meeting DOE hydrogen storage targets at moderate temperature will have significant engineering advantages for mobile applications, as temperature of operation has implications for system weight.

Approach

The project relates to materials development and optimization of catalyst, surface chemistry, crystal and pore structure, and system parameters for the hydrogen spillover phenomenon. To optimize catalyst, platinum nanoparticle wet precipitation method [5] was used to get better metal dispersion. For surface chemistry, different MMOFs were mixed with catalyst to test hydrogen storage and the effect of functional groups. In addition, acid, base, and high temperature after-treatments were used in metal/carbon catalyst systems to have various surface functional groups and to test hydrogen uptake afterwards. We also scrutinized the effect of MMOF structural change on spillover hydrogen adsorption via different mixing strategy with Pt/C catalysts. The project is currently exploring materials without bridging, as bridging has unknown effects on the surface chemistry and structural parameters we hope to optimize.

As discrepancy and debates in spillover hydrogen storage arise, we have spent considerable effort improving our differential volumetric measurement method for better precision and accuracy. We have demonstrated that simple differences in data processing, volume calibration, pumping, and He blank treatment have a drastic effect on the precision of measurement. Validation against published data [6] for GX-31 superactivated carbon and multiple measurements for PtC/IRMOF8 demonstrates better reliability. Moreover, in situ high-pressure spectroscopy is currently being incorporated into the project to characterize spilled over atomic hydrogen.

Results

The measurement instrument employed for our sorption studies is a custom-built volumetric differential Sievert's apparatus with two high-accuracy pressure transducers; an absolute pressure transducer and a differential pressure transducer. Single-sided Sievert's apparatus are broadly used in hydrogen adsorption measurements [7], and a differential unit provides greater accuracy due to simultaneous collection of a blank, a measurement that is highly insensitive to temperature gradients, and generally a higher accuracy of the differential pressure reading relative to the absolute pressure reading. In all volumetric methods, the moles adsorbed are calculated via a mass balance, assuming mass loss from the gas phase is solely due to adsorption to the sample. The accuracy of the measurement relies on an accurate volume calibration, which in turn, relies on the accuracy of the pressure transducers. At 80 bar, 298 K, 100 mg sample measurement, the 'base' error in the measurement of our system (based on mathematical propagation of error using measured variations in volume calibration) is 1 ± 0.6 wt%, which would also be typical for a single-sided measurement. By using the more accurate differential pressure-transducer to calibrate the volume, the error is reduced 12-fold to 1 ± 0.05 wt% (obtained by error propagation with the same inputs, but different operating equation). Nonetheless, since high pressure He is used in this new improved method, it is expected to be prone to systematic error if He adsorbs or if trace residual H_2 is present in the system. The latter may lead to large error for spillover samples, so we are developing a new method that circumvents the high-pressure He calibration, but with a precision of the same level. Current data reported herein is subject to possible He adsorption and/or H_2/He cross-contamination and thus represents highly conservative values. All the methods were validated against published data for GX-31 [8].

Reports from Tsao et al. and Yang et al. [9] state that small catalyst size (d<2 nm) is essential for high uptakes via spillover. For a better platinum dispersion in Pt/C catalysts, wet precipitation method was used as described in a recent publication [5]. Platinum on carbon Maxsorb (Pt/M) was synthesized with good metal dispersion and it confirms the spillover hydrogen uptake data (0.97 wt% at 71 bar, 300 K) published by Yang et al. [5].

With commercial Pt/C and custom synthesized Pt/M, we focused on reproducibility, preparation, and introduction of oxygen functional groups of MMOFs mixed with catalysts. In IRMOF-8 series, different ball milling ratios were used to alter structure. X-ray diffraction (XRD) of the resulting materials shows subtle difference, which can be attributed to damage induced from the mixing procedure [10]. The highest uptake was observed for a material with distorted–but still intact–XRD. Improved catalyst (Pt/M versus commercial Pt/C) did not consistently increase uptake of the mixed PtM/IRMOF8 (Table 1 and Figure 1), suggesting our current mixing procedure is insufficient for spillover to populate the IRMOF8. Thus, methods by which to directly incorporate catalysts into various MMOF structures are in progress. Also, frameworks made solely of strong M-O bonds are being developed which prove to have significantly enhanced thermal and water stability. We are currently exploring MMOFs with incorporated NH_2 groups, which serve as an anchoring site for direct metal-doping for H_2PtCl_6 [11]. Separately, carbonyl or hydroxyl groups functional groups were induced into MMOFs (MMOF=O and MMOF-OH) to test the role of these groups on spillover. After mixing, subtle changes are seen in XRD, but MMOFs remains largely intact. The adsorption amounts are still low (Table 1), but changes in MMOF surface chemistry is not likely to increase uptake until the catalyst MMOF interfacial contact issue can be addressed.

We also examined the effect of surface chemistry on carbon, when carbon serves as the receptor in primary spillover materials. Surface chemistry on Maxsorb was varied using different after-treatments, including high temperature anneal, acid oxidation, and basic oxidation. The removal or increase of surface oxygen groups affected the size of the supported metal: oxidation increased metal crystal size and reduced dispersion (Figure 2a), in certain cases, cations led to pre-precipitation of Pt particles and led to large metal particles. The best uptake achieved for this series of materials was 1.0 wt% for Pt/M_V (Table 1), which is a material that has been annealed to remove oxygen groups. The uptake represents a 22% increase over the undoped Maxsorb precursor.

A Pt-doped activated carbon (Pt/C-INER) provided by C.S. Tsao (INER, Institute of Nuclear Energy Research, Taiwan) showed high low-pressure gravimetric uptake of H_2 (i.e. 1.2 wt% at 298 K and 1 bar [measured at Penn State]; >5 wt% at 69 bar and 298 K [measured in Taiwan] [9]). It was used to probe the interactions between the carbon surface and dissociated hydrogen (H*) when the H* was

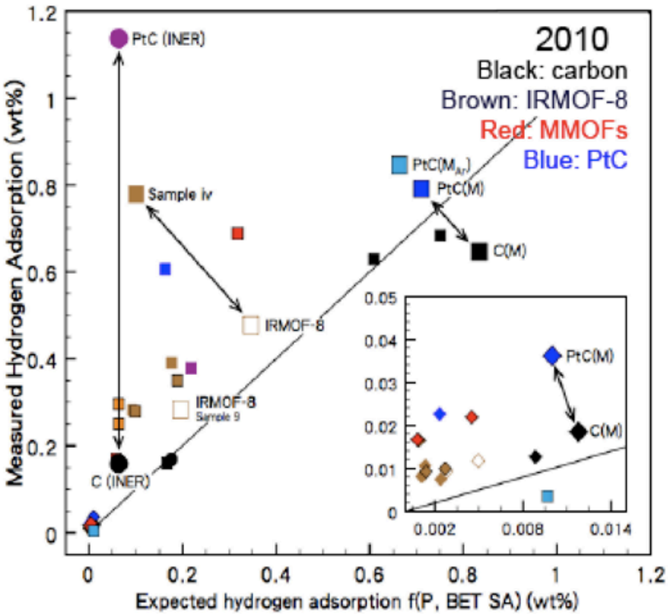

FIGURE 1. Summary of all 2010 H_2 uptake data (excess; relative to He blank at same conditions). H_2 uptake is plotted against uptake "Expected adsorption", which assumes uptake is linearly proportional to both surface area and pressure, i.e. an adapted Chahine Rule [12]. Data is plotted in this way to summarize multiple data at various adsorption pressures in one plot. MMOF samples (IRMOF8 in brown; modified surface chemistry in red) are physically mixed with PtC catalyst. Arrows are used to connect undoped precursor samples with those with catalyst, e.g. carbon (black) and Pt-doped carbon (blue).

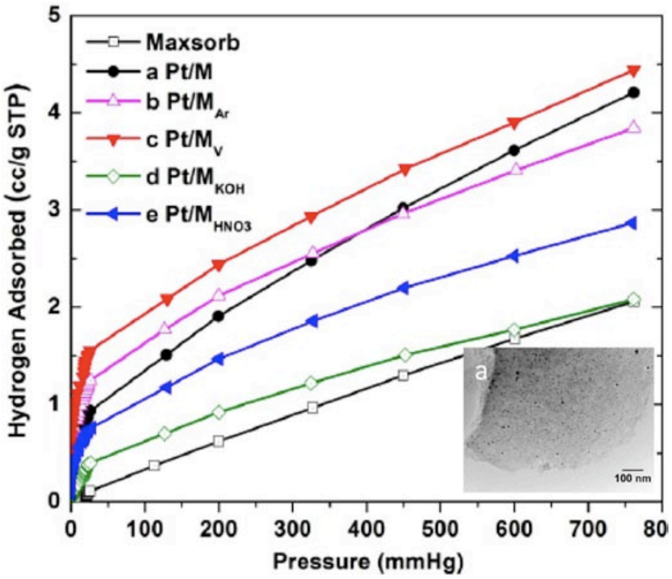

FIGURE 2. Effect of carbon surface chemistry on metal dispersion (low-pressure knee) and low-pressure H_2 isotherms at 1 bar for: (M) Maxsorb (M) activated carbon (a) Pt-doped M, following procedures of Yang et al.; (b) Pt/M_{Ar}: M is annealed at 950°C in Ar prior to Pt-doping; (c) Pt/M_V: M is anneled in vacuum at 1,000 K for 3 hours prior to Pt-doping; (d) Pt/M_{KOH}: M is oxidixed with KOH prior to Pt-doping; (e) Pt/M_{HNO3}: M is oxidized with concentrated (~70%) HNO_3 prior to Pt-doping. Inset (a): transmission electron microscope image of Pt/M shows high dispersion, which was not obtained prior to following the doping procedure of Yang et al.

provided by the adjacent Pt catalyst. In situ Raman (514 nm, 2 mW) measurements of Pt/C-INER were conducted within a silica fiber (wall thickness of 30 µm and center hole of 100 µm; see right, Figure 3) to allow for sequential He and H_2 gas exposures with intermittent degas). A series of sequential He and H_2 exposures were then performed, with a 72 hour vacuum degassing process at 300 K with the turbo pump between each gas introduction (Figure 3). Pt/C-INER in He shows features characteristic of a solid carbon, including a D-band (~1,350 cm^{-1}), G-band (~1,590 cm^{-1}). After He removal and pumping, Pt/C-INER in H_2 at the same spot shows additional bands at 1,180cm^{-1}. These new features vanish after H_2 gas is removed under vacuum and refilled with He gas at room temperature and reappear on a second H_2 exposure. The features were not found in Pt, activated carbon precursor, unactivated carbon, or fiber. Thus, the features at 1,180 cm^{-1} are consistent with a hydrogen spillover process, and given the frequency, can be assigned to a wagging mode coming from weakly bonded atomic hydrogen and the carbon substrate.

Conclusions and Future Directions

- Improvements are made in differential volumetric measurements. Current accuracy is at least 1 ± 0.05 wt% when a 100 mg sample is used.
- Pt-doped AC provided by INER had high uptake at low pressure (1.2 wt% at 1 bar), demonstrating continued promise of spillover mechanism.
- In situ spectroscopy for Pt/AC-INER shows a reversible Raman feature at 1,180 cm^{-1} in hydrogen only, associated with C-H chemical bond. The mode is reversible when H_2 is removed at 298 K. Reversibility is dependent upon carbon structure.
- Type and form of oxygen groups on carbon substrate affects Pt particle size and ultimate spillover.
- Current studies for spillover to MMOF are limited by interfacial contact. Future work will focus on methods to direct dope MMOFs with catalyst. MMOF structure is also an important parameter is obtaining uptake via spillover, and is dictated by mixing technique.
- Future work will explore new methods to facilitate catalyst-carbon-MMOF contact, including doping of MMOF-NH2; effect of particle size; addition of terminal ligand/solvent for surface amino modification for catalyst anchoring; addition of carbon aerogel for pre-formed bridge.
- Future work will alter MMOF structure to introduce high density hydrogenation sites, open metal sites and separately, introduce holes that may facilitate spillover.

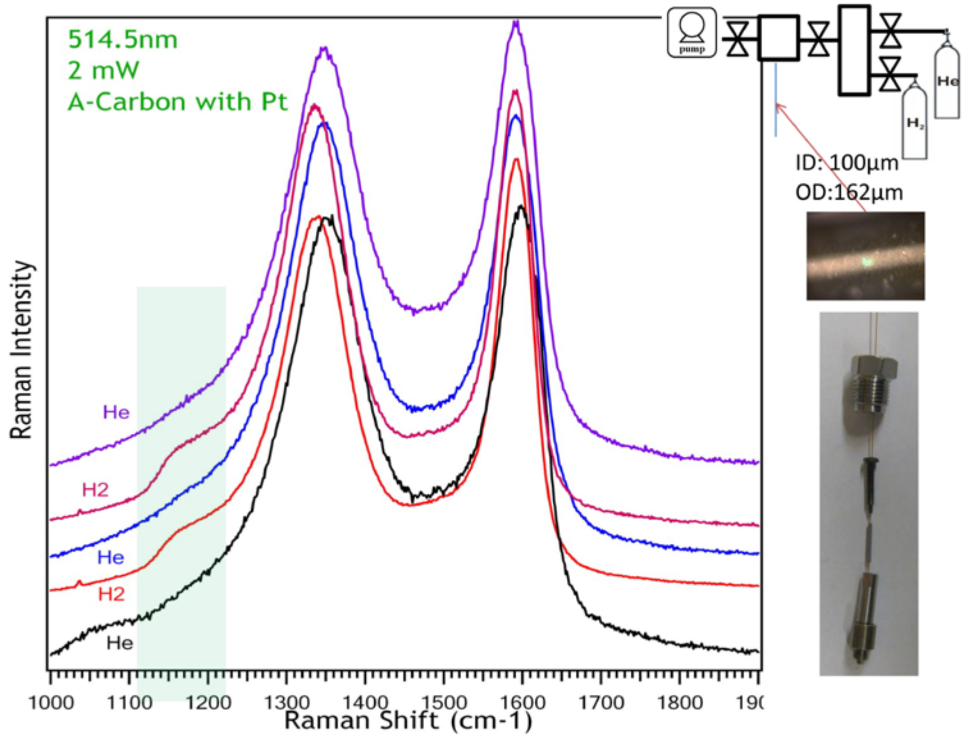

FIGURE 3. Raman spectra of Pt/C-INER at 298 K in a fiber (A) showing D-band (~1,350 cm^{-1}), G-band (~1,590 cm^{-1}), 2D-band (2,700 cm^{-1}) and a D+G band(~2,940 cm^{-1}), exposed sequentially (after intermittent degas at 298 K) to (a) He gas (b) H_2 (c) He (d) H_2, and (e) He. Reversible bands at 1,180 and 2,500 cm^{-1} are seen only in the presence of H_2 gas, and are removed after pressure reduction at 298 K (B).

- Future work will include a systematic study of introduced functional groups on MMOF-4,4’-bypyridine series with in situ spectroscopy.
- Write and submit papers on: (1) methods validation and reproducibility in differential volumetric analyzer; (2) hydrogen spillover on PtC/CuBTC; and (3) variation of MMOF structure/chemistry with secondary spillover studies.

FY 2011 Publications/Presentations

1. A. Lueking, J. Li, M.W. Cole, Four Quarterly Reports, FY2011; Annual Report, FY2011.

2. A. Lueking, Presentation at 2011 Hydrogen Program Annual Merit Review Meeting, May 12, 2011.

3. X.M. Liu, Y.J. Tang, E.S. Xu, T. Fitzgibbons, H.Y. Chuang, H.R. Gutierrez, M.S Yu, C.S. Tsao, J.V. Badding, V.H. Crespi, A.D. Lueking, In-Situ Micro Raman Detection of Reversible Basal Plane Hydrogenation in Pt-doped Activated Carbon, In Preparation.

4. C.-S.Tsao, Y. Liu, H.-Y.Chuang, H.-H. Tseng, T.-Y. Chen, C.-H. Chen, M.-S.Yu, Q.Li, A. Lueking, S.-H. Chen, Submitted to Journal of the American Chemical Society 2011.

5. Lee, J.Y.; Wu, H.H.; Li, J. “Enhancing Hydrogen Adsorption Properties of Microporous Metal Organic Frameworks (MMOFs) by Tuning Their Crystal and Pore Structures”, *Intl. J. Hydro. Ener.*, Submitted.

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