IV.C.1h Hydrogen Storage by Spillover

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Objectives

- To achieve the 6 wt% storage target at room temperature by 2009 by using nanostructured carbons or other sorbents such as metal organic frameworks (MOFs) aided by hydrogen spillover.
- To develop a mechanistic understanding for hydrogen spillover that leads to hydrogen storage.

Technical Barriers

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

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

Technical Targets

To develop hydrogen storage materials with capacities in excess of 6 wt% at room temperature:

- To develop and optimize our new bridge-building techniques for spillover to enhance hydrogen storage.
- To develop direct metal doping technique on carbons for maximal spillover storage.

- To develop synthesis methods for ultrahigh surface area carbons ($>3,500$ m^2/g).
- To obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for hydrogen storage.

Accomplishments

- Using the simple technique for bridge-building, we have studied the spillover storage of the most promising MOFs. It was found that the heats of adsorption for spillover depends on the metal content of the MOF and that the spillover storage depends on both Brunauer-Emmett-Teller (BET) surface area and the heat of adsorption.
- Developed a thermal reduction technique for metal doping on carbon that significantly increased the spillover storage for metal-doped carbon.
- The ambient temperature desorption rates for spillover hydrogen on both bridged MOFs and metal-doped carbon exceeded the DOE discharge rate target (0.02 g/s/kW).
- Deuterium isotope tracer study showed direct evidence that (1) hydrogen atoms are formed in spillover storage and (2) desorption follows a reverse spillover route.
- Developed a plasma post-treatment technique for metal-doped carbon that significantly increased the spillover storage capacity.

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Introduction

A fundamental study of the structure-property relationships of MOFs for hydrogen storage by spillover is needed. Through such a study, the structural and surface characteristics that most strongly influence the H$_2$ adsorption capacity of MOFs by spillover may be elucidated and such results will provide a direction for future studies.

Nanostructured carbons have tremendous potential for spillover-storage at ambient temperature. An added and important benefit for carbon is that carbon is more stable than MOFs. The theoretical limit for spillover-storage on carbon is >8 wt% for a carbon with a BET surface area of 4,000 m^2/g. We are developing the most effective metal doping technique in order to maximize spillover-storage.
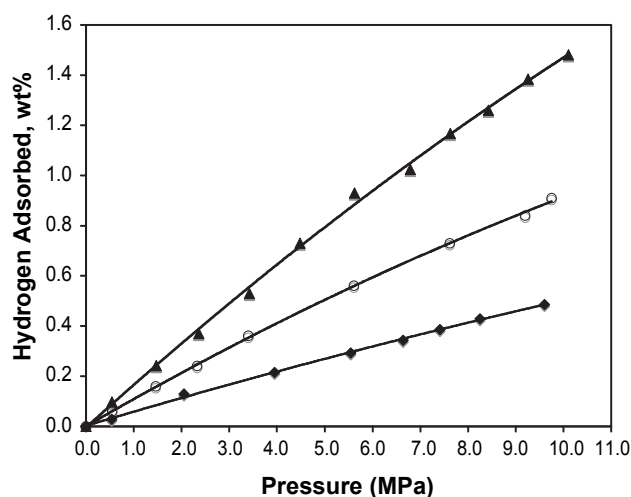
Approach

We have chosen the most promising MOFs and the MOFs that contain different metal oxide clusters for this work so a systematic understanding can be obtained. We have prepared bridged MOFs with added catalyst and studied the spillover-storage characteristics at 298 K.

We are using the templating approach to develop ultra-high surface area carbons. Using these carbons, we are developing most effective metal doping techniques for spillover-storage.

Results

We have studied spillover-storage on COF-1, HKUST-1, MIL-101, MOF-177 and IRMOF-8. A typical result is shown for MIL-101 in Figure 1. It is seen that the storage capacity for pure MIL-101 was about 0.4 wt% at 10 MPa and 298 K. The capacity was nearly doubled by mixing with 10 wt% added catalyst (5 wt% Pt/activated carbon), and it was further increased to 1.5 wt% storage by adding 10% carbon bridges between the MOF and the catalysts. As shown previously, the isotherms for all bridged MOFs were reversible at 298 K. The simple bridge-building technique has been described in previous reports.

The isosteric heats of adsorption for the bridged MOFs were measured based on the temperature dependence, shown in Figure 2. It is seen that the heats of adsorption depended on the metal content. COF-1 had no metal and had the lowest $-\Delta H$. IRMOF-8 and MOF-177 had the same metal oxide clusters ($[Zn_4O]^{6-}$), while IRMOF-8 had a higher metal content, and showed higher $-\Delta H$. The metals were Cr for MIL-101 and Cu for HKUST-1.
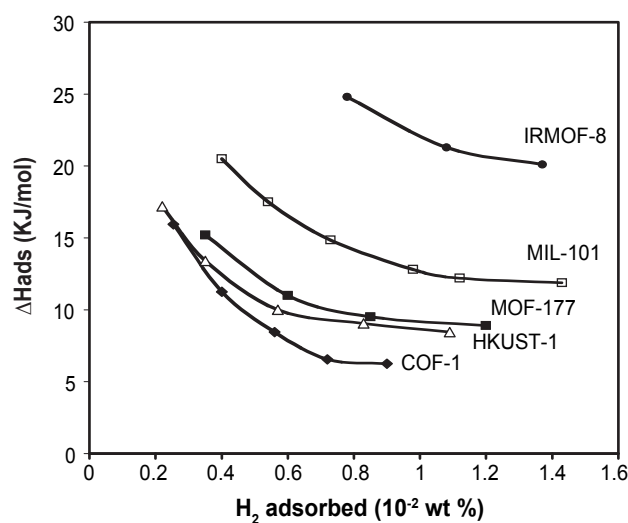
The results for MOFs and bridged MOFs are summarized in Table 1. From this table it is clear that both BET surface area and $-\Delta H$ are important in determining the spillover storage capacity.
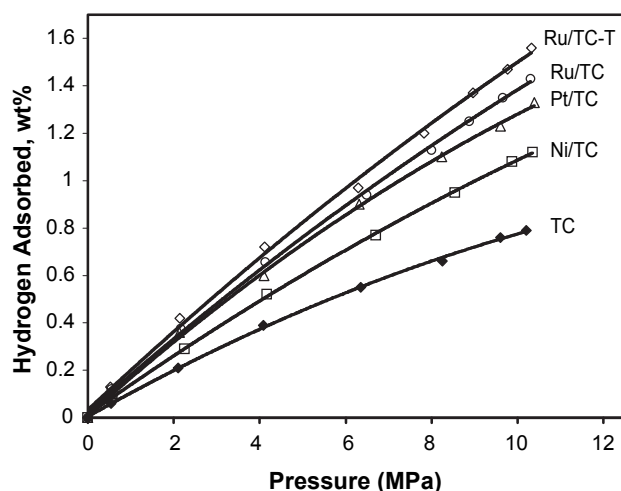
TABLE 1. Summary Results on Pure and Bridged MOFs (Bridged MOFs: 10% Pt/AC + 80% MOF with 10% Carbon Bridges)

	BET Surface Area, m^2/g	H_2 at 77 K, 1 atm, wt%	H_2 at 298 K, 100 atm, wt%	Bridged MOF, H_2 at 298 K, 100 atm, wt%	ΔH, Bridged, kJ/mol
IRMOF-8	548	1.4	0.4	2.2-4.0	-21
COF-1	628	1.1	0.3	0.7	-7
HKUST-1	1296	2.2	0.3	1.1	-9
MIL-101	2930	1.8	0.5	1.5	-13
MOF-177	3100	1.5	0.6	1.5	-10

Using the templating approach, and using EMC-2 zeolite as the template (developed at Mulhouse University, France), a nanostructured carbon with a BET surface area of 3,839 m^2/g was synthesized. The carbon was doped with nanoparticles of different metals (Ru, Pt and Ni). The spillover storage isotherms at 298 K are shown in Figure 3. The storage capacities for the doped carbons followed the order of the hydrogen isotherms on pure metal powders: Ru > Pt > Ni. The doped samples were subjected to the standard H_2 reduction post-treatment: 300°C in H_2. We then used a high temperature thermal reduction technique for

FIGURE 1. H_2 Isotherms at 298 K on MIL-101 bridged with 10% added catalyst (5%Pt/AC): MIL-101 (◆); physical mixture of 90% MOF and 10% Pt/AC (○); bridged sample with 10% carbon bridges (▲).

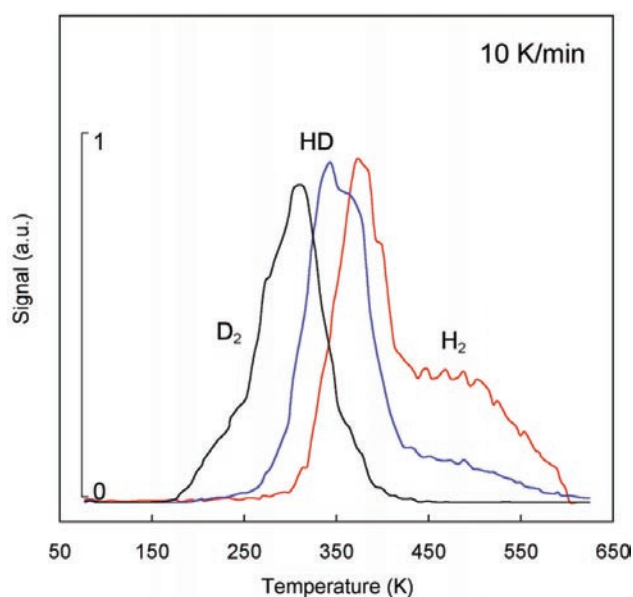**FIGURE 2.** Isosteric heats of adsorption of H_2 on bridged metal-organic frameworks with 10% Pt/carbon.

FIGURE 3. H_2 isotherms at 298 K on TC and 6 wt% metal-doped (ultrasound assisted) M/TC. All M/TC were H_2-reduced at 300°C except Ru/TC-T was thermally reduced (in N_2) at 900°C (1 hr). BET surface area (m²/g): Ru/TC-T = 2,090; Ru/TC = 3,004; Pt/TC = 3,120; Ni/TC = 3,091; TC = 3,839.

FIGURE 4. TPD Result for 6 wt% Pt on TC (3,400 m²/g) after dosing with 0.4 atm H_2 followed by D_2 at 298 K for 5 min (followed by quench, gas phase removal and TPD).

the post-treatment: 900°C in N_2 (1 hr), marked by Ru/templated carbon (TC)-T in Figure 3. Although the BET surface area of this sample was reduced by nearly 50% because of the high temperature treatment, the spillover storage capacity was significantly increased. Further examination of the samples showed that the metal nanoparticles were anchored deeper into the carbon surface by the thermal reduction step, hence more spillover.

In order to obtain a better understanding for the spillover storage mechanism, deuterium isotope tracer and temperature programmed desorption (TPD) studies were performed on a Pt/TC sample. The Pt/TC sample was subjected to sequential dosing of H_2 and D_2 at 298 K, followed by quenching in liquid N_2, shallow evacuation and TPD. Typical results are shown in Figure 4. In this run, 0.4 atm H_2 was dosed first for 5 min at 298 K, followed by dosing with 0.4 atm D_2 for 5 min. The TPD result is shown in Figure 3. The TPD result showed clear desorption peaks of D_2, HD and H_2, in the reversed sequence of dosing. Importantly, a large desorption peak of HD occurred. Detailed results on calibration experiments, other dosing sequences, etc. are shown elsewhere [1]. The results are direct evidence to show that (1) atomic species are formed during spillover storage, and (2) the desorption step follows a reverse spillover process, i.e., atoms migrate back to the metal particle, on which to recombine and desorb as molecules.

Conclusions and Future Directions

Conclusions

- H_2 dissociation and spillover can significantly increase the H_2 storage capacity at ambient temperature for all MOFs and nanostructured carbons.
- Spillover-storage on MOFs depends on both surface area and binding energy.
- Spillover-storage on nanostructured carbons depends on how metals are doped, and is far from reaching theoretical limits.
- Desorption rates at ambient temperature for both MOFs and carbon exceed DOE target for discharge rate.
- Deuterium isotope tracer studies showed direct evidence for hydrogen dissociation and spillover at 298 K.
- Deuterium isotope tracer studies also showed that desorption followed a reverse spillover mechanism.

Future Directions

- Storage by spillover with bridge-building on other high surface area MOF including PCN-type MOFs (MOFs synthesized by Joe Zhou) from our Center, Mn^{2+} MOFs.
- New direct doping techniques on AX-21 and other ultra-high surface area carbons.

- Obtain basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope.
- To achieve DOE weight and volumetric targets and address issues on fueling rates and other DOE targets.

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