

IV.C.1b A Biomimetic Approach to Metal-Organic Frameworks with High H₂ Uptake

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Objectives

- Design, synthesis, and characterize high-surface-area metal-organic frameworks (MOFs) with active metal centers aligned in porous channels and accessible by H₂ molecules.
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H₂.
- These MOFs can help to reach the DOE 2010 and ultimately 2015 hydrogen storage goal.

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:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

- The focus of the proposed research is the use of concepts evident in metalloproteins to guide the synthesis of MOFs with gas-adsorption affinity around 15 to 20 kJ/mol for hydrogen and high surface area.

- The overall objective is to achieve the DOE 2010 and 2015 system goals, primarily the gravimetric and volumetric storage goals, at or near ambient temperatures and moderate pressure for on-board vehicular hydrogen storage (Table 1).

Accomplishments

- Synthesized 50 new ligands for MOF formation.
- Evaluated the contribution to hydrogen adsorption from catenation in MOFs.
- Studied the effect of a variety of open metal centers on hydrogen affinity of the MOFs.
- Explored double-bond containing ligand and its influence on hydrogen adsorption.
- Discovered a general way toward MOFs with extremely high surface area: incorporation of mesocavities with microwindows.

TABLE 1. System Targets: On-Board Hydrogen Storage for Light-Duty Vehicles

Storage Capacity	Units	2010	2015	Ultimate	Texas A&M (excess, sorbent-based)	
Gravimetric: net useful H ₂ /max system mass	kg H ₂ /kg system	0.045	0.055	0.075	0.072 77 K, 50 bar	0.009 298 K, 50 bar
Volumetric: net useful H ₂ /max system volume	kg H ₂ /L system	0.028	0.040	0.070	0.040 77 K, 50 bar	0.005 298 K, 50 bar



Introduction

In the past decade, there has been an escalation of interest in the study of MOFs due to their fascinating structures and intriguing application potential. Their exceptionally high surface areas, uniform yet tunable pore sizes, and well-defined adsorbate-MOF interaction sites make them suitable for hydrogen storage. Various strategies to increase the hydrogen capacity of MOFs, such as using pore size comparable to hydrogen molecules, increasing surface area and pore volume, utilizing catenation, and introducing coordinatively unsaturated metal centers (UMCs) have been widely explored to increase the hydrogen uptake of the

MOFs. Recently, inelastic neutron scattering (INS) and neutron powder diffraction as well as computational studies suggest that the choice of both metal centers and ligands can play an important role in tailoring the gas-framework interactions. Additionally, those ligands containing phenyl rings have been proven favorable for hydrogen adsorption. MOFs with hydrogen uptake approaching the DOE 2010 gravimetric storage goal under reasonable pressure but cryo-temperature (typically 77 K) were reported. However, the weak interaction between hydrogen molecules and MOFs has been the major hurdle limiting the hydrogen uptake of MOFs at ambient temperature.

Approach

Our strategy to enhance H₂ uptake was as follows: (1) Prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. (2) Synthesized porous MOFs with high hydrogen adsorption affinities based on different coordinatively UMCs. (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. (4) Obtained stable MOFs with high surface areas by the incorporation of mesocavities with microwindows.

Results

In the past year, we have prepared a series of MOFs and explored their applications in hydrogen storage. Table 2 shows the comparison of hydrogen uptakes of selected MOFs. Next we will discuss in detail the results of H₂ uptakes of these MOFs.

(a) Catenation Isomer Pair of MOFs

Catenation, the intergrowth of two or more identical frameworks, has long been an interesting topic in MOF research. It can be utilized as an alternative way to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs. Recently, we developed a templating strategy to control catenation/noncatenation in porous MOFs, obtained the catenation isomer pair of PCN-6 and PCN-6', and were able to quantitatively evaluate the contribution from catenation to the hydrogen uptake of a MOF material (Figure 1). Our studies revealed that catenation can lead to a 41% improvement of apparent Langmuir surface area (3,800 m²/g for PCN-6 vs 2,700 m²/g for PCN-6'), a 29% increase in excess gravimetric hydrogen uptake (1.74 wt% for PCN-6 vs 1.35 wt% for PCN-6') at 77 K/760 torr, and a 133% increase in volumetric hydrogen uptake (9.19 kg/m³ for PCN-6 vs 3.49 kg/m³ for PCN-6') in the catenation isomer pair of PCN-6/PCN-6'. The study of isosteric heats of adsorption indicated that catenated PCN-6

and noncatenated PCN-6' have similar hydrogen-adsorption enthalpies at low coverage (6.2 kJ/mol for PCN-6 vs 6.0 kJ/mol for PCN-6'). However, as the hydrogen loading increases, PCN-6 exhibits steadily higher hydrogen-adsorption enthalpies than those of PCN-6'. INS spectroscopy studies revealed that the first sites occupied by H₂ are the open Cu centers of the paddlewheel units in both PCN-6 and PCN-6'. However, in PCN-6, there exist three specific H₂-binding Cu sites while PCN-6' possesses only one. At high hydrogen loadings, the interaction between H₂ molecules and the organic linkers is stronger in catenated PCN-6 than that in noncatenated PCN-6'. Such a stronger interaction resulted in more effective hydrogen binding sites in catenated PCN-6. Hydrogen sorption studies up to 50 bar demonstrated that catenation can lead to higher hydrogen uptake in MOFs even at high pressure. For example, the excess hydrogen uptake of catenated PCN-6 is 72 mg/g (6.7 wt%) at 77 K/50 bar or 9.3 mg/g (0.92 wt%) at 298 K/50 bar, and that in noncatenated PCN-6' is 42 mg/g (4.0 wt%) at 77 K/50 bar or 4.0 mg/g (0.40 wt%) at 298 K/50 bar. Importantly, PCN-6 exhibits a total hydrogen uptake of 95 mg/g (8.7 wt%) (corresponding to 53.0 g/L) at 77 K/50 bar and 15 mg/g (1.5 wt%) at 298 K/50 bar. Significantly, the deliverable (50 to 1.5 bar) hydrogen capacity of PCN-6 is 75 mg/g (or 41.9 g/L) at 77 K/50 bar, showing its great potential as a cryogenic hydrogen-storage medium.

TABLE 2. Comparison of Hydrogen Uptakes of Selected MOFs

Material	ΔH_{ads} (kJ/mol)	H ₂ Adsorption			
		Gravimetric H ₂ uptake (wt%)	Volumetric H ₂ uptake (g/L)	T (K)	P (bar)
PCN-6	6.2~4.5	7.2	40.2	77	50
		1.90	10.6	77	1.0
		0.92	5.14	298	50
PCN-6'	6.0~3.9	4.2	11.8	77	50
		1.62	4.73	77	1
		0.40	1.12	298	50
(Co) PCN-9 (Fe) (Mn)	10.1	1.53	14.1	77	1
	6.4	1.06	9.60	77	1
	8.7	1.26	11.3	77	1
PCN-61	9.3~4.5	4.28	14.8	77	16
		2.11	7.32	77	1
		0.65	2.25	298	109
PCN-66	7.2~4.5	1.69	4.26	77	1

(b) Porous MOFs with Different UMCs

The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen. Recent theoretical calculations suggested that the H₂-open metal center interactions may be tuned by

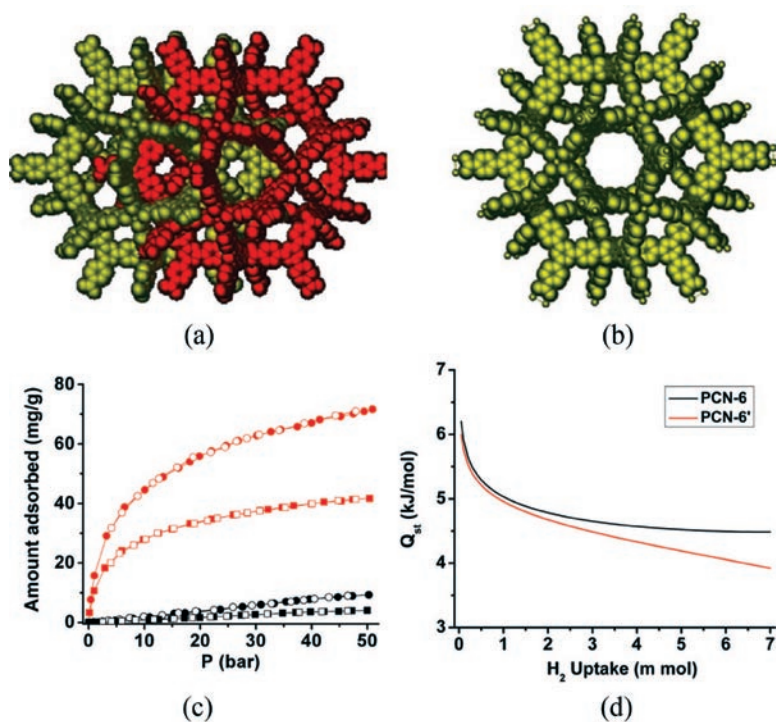


FIGURE 1. (a) The framework of catenated PCN-6. (b) The framework of noncatenated PCN-6'. (c) Excess hydrogen sorption isotherms of PCN-6 and PCN-6' at 77 (red) and 298 K (black): circles, PCN-6; squares, PCN-6'; solid symbols, adsorption; open symbols, desorption. (d) Isothermic heats of adsorption for PCN-6 and PCN-6'.

varying the metal types, and the evaluation of different UMCs' affinities to hydrogen molecules will be very instructive for the future design of porous MOFs with high hydrogen adsorption capacities, especially at near ambient temperatures. Herein, we prepared three isostructural porous MOFs, designated as PCN-9 (Co), PCN-9 (Fe) and PCN-9 (Mn), respectively. To test the permanent porosities of the three porous MOFs, N_2 sorption isotherms were measured at 77 K. All of them exhibit type-I sorption behavior, as expected for microporous materials. Derived from the N_2 sorption data, the Brunauer-Emmett-Teller (BET) surface areas are 1,064 m^2/g (Langmuir surface area, 1,355 m^2/g), 682 m^2/g (Langmuir surface area, 848 m^2/g), and 836 m^2/g (Langmuir surface area, 1,057 m^2/g) for PCN-9 (Co), PCN-9 (Fe), and PCN-9 (Mn), respectively. H_2 sorption measurements at 77 K were also carried out to check their hydrogen storage performances. At 77 K and 760 Torr, the hydrogen uptake capacity of PCN-9 (Co) is 1.53 wt%, and PCN-9 (Fe) can adsorb 1.06 wt% hydrogen, while PCN-9 (Mn) can uptake 1.26 wt% hydrogen. The H_2 affinities of the three porous MOFs have been estimated by isosteric heats of adsorption (Q_{st}). PCN-9 (Co) has a Q_{st} of 10.1 kJ/mol and PCN-9 (Mn) has a Q_{st} of 8.7 kJ/mol, while PCN-9 (Fe) has a relatively lower Q_{st} of 6.4 kJ/mol. These results revealed that the Co UMC possesses a higher hydrogen affinity

compared to the Fe and Mn UMCs, indicating that the implementation of open Co centers into porous MOFs may be a promising way to enhance hydrogen adsorption enthalpies for near-ambient hydrogen storage application.

(c) MOFs Based on Double-Bond-Coupled Di-Isophthalate Linkers

While ligands containing phenyl rings have been proven favorable for hydrogen adsorption, those containing double-bond functionalities have rarely been studied in gas adsorption MOFs. Herein, we present hydrogen storage studies in MOFs containing nanoscopic cages based on two predesigned double-bond-coupled bis(isophthalate) ligands: azobenzene-3,3',5,5'-tetracarboxylate (abtc) and transstilbene-3,3',5,5'-tetracarboxylate (sbtc). Solvothermal reactions of $Cu(NO_3)_2$ with H_4aobtc or H_4sbtc give rise to isostructural PCN-10 and PCN-11, respectively. The enduring porosity of PCN-10 and PCN-11 is confirmed by gas adsorption studies. The N_2 adsorption isotherms of the activated samples exhibit type-I sorption behavior with a Langmuir surface area of 1,779 or 2442 m^2/g , corresponding to

a BET surface area of 1,407 or 1,931 m^2/g and a total pore volume of 0.67 or 0.91 mL/g for PCN-10 or PCN-11, respectively. In particular, both contain nanoscopic cages that are particularly suitable for gas storage. At 760 Torr and 77 K, the excess hydrogen uptake of PCN-10 is 2.34 wt% (18.0 g/L) and that of PCN-11 is as high as 2.55 wt% (19.1 g/L). When the pressure is increased, the excess adsorption at 77 K saturates around 20 atm and reaches values of 4.33% (33.2 g/L) and 5.05% (37.8 g/L) for PCN-10 and PCN-11, respectively. Gas adsorption experiments suggest that MOFs containing C=C double bonds are more favorable than those with N=N double bonds in retaining enduring porosity after thermal activation, although the N=N double bond has slightly higher H_2 affinity.

(d) MOFs with the Incorporation of Mesocavities and Microwindows

Polyhedron-based MOFs may lead to higher stability and porosity if the sizes of the open windows of the polyhedra are limited. Herein we report a strategy for stabilizing MOFs with high surface areas by introducing mesocavities with microwindows into the MOFs based on the (3,24)-connected network. The nanoscopic hexatopic carboxylate

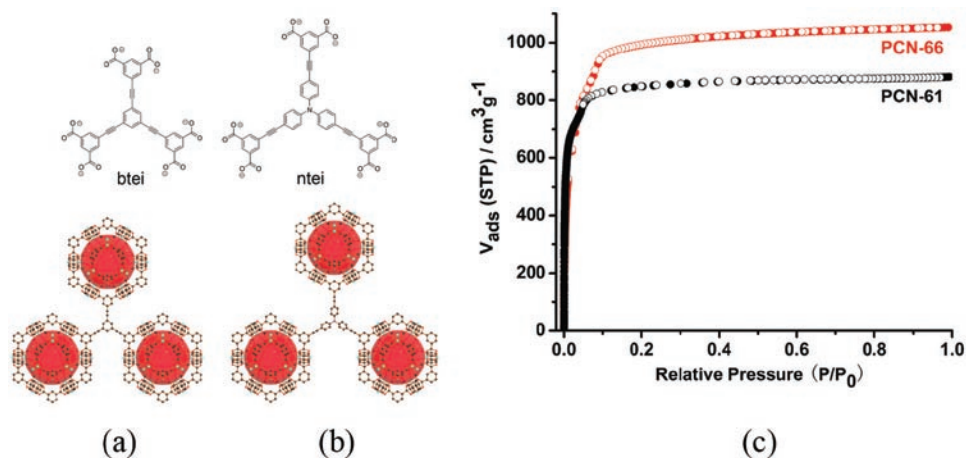


FIGURE 2. (a) Nanoscopic ligand btei and cuboctahedra as structural building units in PCN-61. (b) Nanoscopic ligand ntei and cuboctahedra as structural building units in PCN-66. (c) N_2 sorption isotherms for PCN-61 (black) and PCN-66 (red) at 77 K. Filled and open circles represent adsorption and desorption data, respectively.

ligands designed for this purpose are 5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate) (btei) and 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))triiisophthalate (ntei) and solvothermal reactions of H_6 btei and H_6 ntei with copper salts yielded two MOFs, PCN-61 and PCN-66 (Figure 2). With the BET model, an activated PCN-61 sample was estimated to have a specific surface area of $3,000 \text{ m}^2 \text{ g}^{-1}$, and the Langmuir surface area was $3,500 \text{ m}^2 \text{ g}^{-1}$ assuming monolayer coverage. For PCN-66, where the larger ligand was used, there was a remarkable increase in surface area (BET, $4,000 \text{ m}^2 \text{ g}^{-1}$ and Langmuir, $4,600 \text{ m}^2 \text{ g}^{-1}$), which supports our hypothesis that the expansion of the ligand leads to increased surface area. To the best of our knowledge, PCN-66 possesses the highest surface area reported to date for MOFs based on paddlewheel clusters. It can be extrapolated that use of even larger hexatopic carboxylate ligands may lead to stable MOFs with even higher surface areas. The high surface area in PCN-61 and PCN-66 prompted us to evaluate their hydrogen adsorption performance. At 77 K and 760 Torr, the excess gravimetric hydrogen uptake capacity of PCN-61 and PCN-66 can reach 2.11 wt% (corresponding to 7.32 g/L) and 1.69 wt% (corresponding to 4.26 g/L), respectively. At higher pressure, the excess hydrogen uptake of PCN-61 is 4.28 wt% (corresponding to 14.8 g/L) at 77 K/16 bar or 0.65 wt% (corresponding to 2.25 g/L) at 298 K/50 bar. The high pressure hydrogen adsorption studies of PCN-66 are currently underway and will be reported next year.

Conclusions and Future Directions

Conclusions

- MOFs containing catenation possess high capacity of hydrogen adsorption.
- MOFs containing UMCs tend to have high hydrogen affinity; MOFs based on different UMCs show different hydrogen adsorption capacities.
- MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers have been proven favorable for hydrogen adsorption.
- MOFs with the incorporation of mesocavities and microwindows exhibit high surface areas and good potential in hydrogen storage.

Future Directions

- Further enhancement of H_2 -MOF interaction by the introduction of higher density of coordinatively UMCs (heat of adsorption 15 kJ/mol).
- Improvement of H_2 uptake at temperatures higher than 77 K by ligand and MOF design.
- Increase MOF thermal stability while maintaining its porosity.
- Preparation of MOFs with high surface area and optimized cage size ($6,000 \text{ m}^2/\text{g}$).

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