IV.C.1b A Biomimetic Approach to Metal-Organic Frameworks with High H$_2$ Uptake

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Objectives

- Design, synthesize, and characterize metal-organic frameworks (MOFs) with active metal centers aligned in porous channels and accessible by H$_2$ molecules.
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H$_2$.
- 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 (3.3.4) of the Fuel Cell 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.

- 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).

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

Storage Parameter	Units	2010	2015	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H$_2$ (net useful energy/max system mass)	kWh/kg (kg H$_2$/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H$_2$ (net useful energy/max system volume)	kWh/L (kg H$_2$/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)

Accomplishments

- Crystal twins with two isomeric phases have been discovered, and gas sorption studies revealed that compared to the β-phase, the α-phase possesses a larger surface area leading to higher hydrogen capacity. This symmetry-preserving isomerization strategy can be applied to other MOFs.
- A MOF, which is based on a polyyne-coupled di-isophthalate linker formed in situ, was constructed. Compared to phenyl rings, the polyyne chains showed improved hydrogen affinity.
- An isoreticular series of MOFs with dendritic hexa-carboxylate ligands tend to have high surface area and stability. PCN-68 has an excess gravimetric H$_2$ uptake of 7.2 wt% at 77 K and 50 bar.
- Porous organic frameworks (POFs) with high surface area and tunable pore size were designed and synthesized. They exhibit promising H$_2$ uptake.

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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 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 desorption. 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 H_2 uptake was as follows: (1) Prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. Catenation can be utilized to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs. (2) Synthesized porous MOFs with high hydrogen adsorption capacities based on different coordinatively UMCs. The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen. (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. Those ligands containing phenyl rings in MOFs have been proved favorable for hydrogen adsorption. (4) Design and synthesis porous MOFs based on an anthracene derivative which can provide additional hydrogen binding sites to increase the hydrogen uptake. (5) Obtained stable MOFs with high surface areas by the incorporation of mesocavities with microwindows. (6) Constructed MOFs with "close-packing" alignment of open metal sites, which can increase the number of nearest neighboring open metal sites of each H_2-hosting void in a three-dimensional framework so that they can interact directly with the guests (H_2 molecules) inside the void. (7) Built up porous lanthanide MOFs and studied their potential application in gas adsorption. (8) Prepared symmetry-preserving isomer pair of MOFs and studied the impact of isomerization on H_2 storage capacity in MOFs. (9) Incorporated polyyne unit into MOFs, which exhibit H_2 affinity higher than that of MOFs containing phenyl rings. (10) Designed and synthesized POFs with chemical stability higher than that of MOFs.

Results

In the past year, we prepared a series of MOFs and POFs and explored their applications in hydrogen storage. Table 2 shows the comparison of hydrogen uptakes of selected MOFs and POFs. Next we will discuss in detail the results of H_2 uptakes of these materials.

TABLE 2. Comparison of Hydrogen Uptakes of Selected MOFs and POFs

Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 uptake (Wt%)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
PCN-16	-	5.10	36.9	77	30
PCN-16′	-	2.90	22.2	77	30
PCN-46	7.20	5.31	34.7	77	32
PCN-61	6.36	5.87 1.70 0.66	35.0 9.63 3.74	77 195 298	33 90 90
PCN-68	6.22	6.23 1.60 0.77	29.6 7.27 3.50	77 195 298	45 90 90
PCN-69	6.09	7.20 1.70 1.00	29.6 6.10 4.10	77 195 298	50 90 90
POF-1	7.59	3.30	-	77	45
POF-2	6.89	3.76	-	77	40
POF-3	5.51	4.28	-	77	42

(a) Symmetry-Preserving Isomer Pair

A symmetry-preserving isomer pair (α phase and β phase NbO-type structures) of MOFs crystallized in the same R-$3m$ space group but with different pore sizes have been discovered, allowing the direct study of the impact of pore size on gas storage capacity in MOFs for the first time (Figure 1a). The α phase MOF (PCN-16) is isostructural with previously reported NbO-type MOFs constructed from tetracarboxylate linkers and has two distinct types of cages. The first consists of 12 ebdc ligands connecting six paddlewheel secondary building units (SBUs) to form an octahedral cage, in which each ligand utilizes only two of its four carboxylate functionalities; half of the ligands join adjacent SBUs through carboxylate groups from the same phenyl ring and half use carboxylates at opposite ends of the ligand. The dimensions of the windows into the cage are about 10×10 Å and 8×8 Å (atom to atom distances). The second type of cages, which is elliptical, is formed from six ebdc ligands connecting twelve paddlewheel SBUs. In this type, each ligand uses all of its four carboxylate groups. The dimensions of the windows into the elliptical cage are also 10×10 Å and 8×8 Å. These two

(a)

α-phase NbO-type

β-phase NbO-type
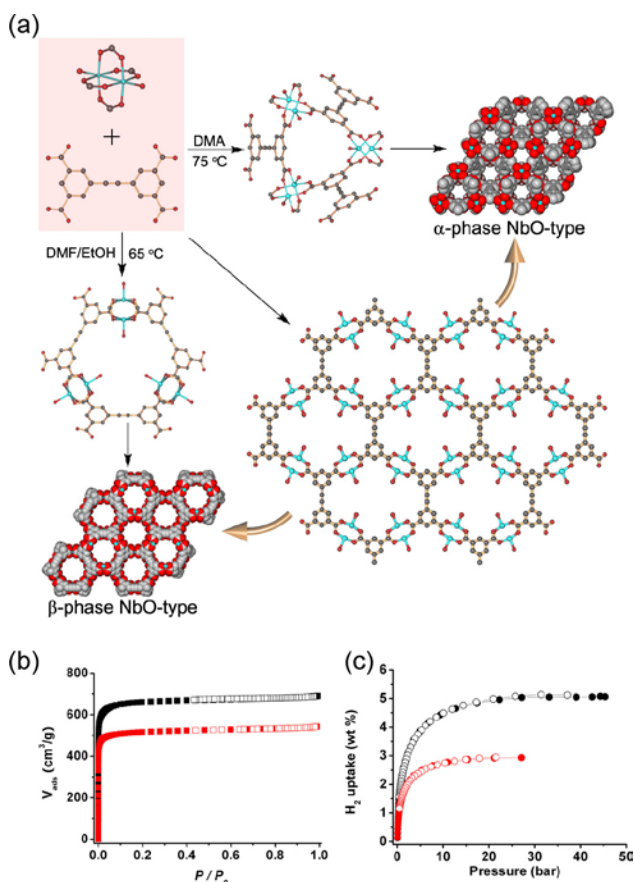
(b)

(c)

FIGURE 1. (a) The formation of the two symmetry-preserving NbO-type phases. (b) N$_2$ sorption isotherms of PCN-16 (black) and PCN-16′ (red) at 77 K. (c) Excess hydrogen sorption isotherms of PCN-16 (black) and PCN-16′ (red) at 77 K.

kinds of cages are connected to each other by sharing three paddlewheel SBUs to result in a three-dimensional framework with the NbO topology. The resulting dimensions of the -3m (in space group R-3m) channels are about 8 × 8 Å along the c-axis consistent with the size of the channels in the previously reported NbO-type MOFs. The solvent accessible volume in the dehydrated structure is 72.5% calculated from PLATON/SOLV. In PCN-16′, however, the channels are larger than those in PCN-16, with the dimensions of 11 × 11 Å. The solvent accessible volume in the dehydrated structure is 70.1% calculated from PLATON/SOLV, which is slightly smaller than that of PCN-16.

To check the permanent porosities of the pair of isomers, N$_2$ sorption isotherms at 77 K were collected for the dehydrated samples. As shown in Figure 1b, both PCN-16 and PCN-16′ display typical Type-I sorption behavior. PCN-16 has a Brunauer-Emmett-Teller (BET) surface area of 2,273 m^2/g (Langmuir surface area, 2,800 m^2/g) and a total pore volume of 1.06 cm^3/g while PCN-16′ possesses a 1,760 m^2/g BET surface area (Langmuir surface area, 2,200 m^2/g) and a 0.84 cm^3/g pore volume.

The differing pore structures as evidenced by the BET surface areas directly impact the adsorption capacities for hydrogen as indicated in Figures 1c, PCN-16 demonstrates significantly higher hydrogen adsorption capacity than PCN-16′. At 77 K and 760 torr, PCN-16 can adsorb 2.6 wt% hydrogen, comparable to the values observed in other α phase NbO-type copper MOFs. In contrast, PCN-16′ can only adsorb 1.7 wt% hydrogen, much lower than that in PCN-16. This difference persists at higher pressures where the excess hydrogen uptake of PCN-16 saturates at 5.1 wt%, while the saturation for PCN-16′ occurs with the value of only 2.9 wt% (Figure 1c).

Because PCN-16 and PCN-16′ are isomers of each other and both crystallize in the same space group and contain similar nanoscopic cages, the superior gas adsorption properties of PCN-16 can mainly be attributed to the pore size, which is smaller than that of PCN-16′. The small pores lead to an increased effective surface area, offering more adsorption sites for hydrogen. Indeed, the saturation uptake of hydrogen at 77 K for each isomer is consistent with the different BET surface areas, as explained in a recent analysis. The results above also suggest that α phase NbO-type copper MOFs should be better for gas storage than their β phase counterparts.

(b) MOF Derived from a Polyyne-Coupled Di-Isophthalate Linker Formed In Situ

The NbO-type MOFs, which consist of 4-connected di-isophthalate ligands and 4-connected secondary building units, have shown excellent framework stability, porosity, and gas adsorption capacity. On the other hand, their hydrogen adsorption capacity at room temperature is relatively low due to weak framework-hydrogen interactions. In our continuing exploration of MOFs as a hydrogen storage medium, double bonds and aromatic rings were studied as possible framework-hydrogen interacting sites. However, prior to this work, carbon-carbon triple bonds, especially polyyne chains, have not been systematically studied for gas adsorption purposes in MOFs. In this contribution, we report an NbO-type MOF (PCN-46) that is constructed based on a polyyne-coupled di-isophthalate ligand formed in situ (Figure 2). The ensuing MOF has permanent porosity after the removal of guest molecules, with a BET surface area of 2,500 m^2 g^{-1} and a uniform pore size around 6.8 Å (Figure 2d). At 77 K and 760 Torr, PCN-46 can reversibly adsorb 1.95 wt% of H$_2$ (Figure 2e). Under high pressure range, the saturated excess gravimetric H$_2$ uptake is 5.31 wt% (56.1 mg g^{-1}) at 32 bar. Taking the gaseous H$_2$ compressed within the void pore at 77 K into consideration, the total gravimetric H$_2$ uptake can reach as high as 6.88 wt% (73.9 mg g^{-1}) at 97 bar. Calculated from the crystal density of the activated form (0.6185 g cm^{-3}), PCN-46 has an excess volumetric
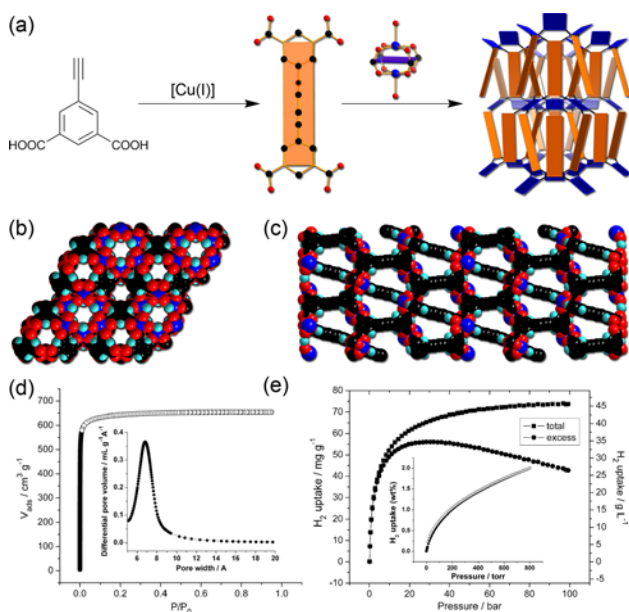
FIGURE 2. (a) In situ formed ligand bdi[4-] and the formation of NbO-type framework. (b) Atomic packing of PCN-46, viewed through [0 0 1] direction. (c) Atomic packing of PCN-46, viewed through [1 0 0] direction. (d) The N_2 sorption isotherm at 77 K (solid symbols, adsorption; open symbols, desorption) and pore size distribution of PCN-46. (e) Gravimetric and volumetric H_2 uptake in PCN-46 at 77 K (solid symbols, adsorption; open symbols, desorption).

H_2 uptake of 34.7 g L^{-1} (32 bar) and a total volumetric uptake of 45.7 g L^{-1} (97 bar).

Based on a variant of the Clausium-Clapeyron equation, the H_2 isosteric adsorption enthalpy of PCN-46 reaches 7.20 kJ mol^{-1} at low coverage, and decreased to 4.06 kJ mol^{-1} at medium coverage. The increased heat of hydrogen adsorption in PCN-46, compared to those of other NbO type MOFs, can be attributed to the interaction between dihydrogen molecules and the exposed and delocalized ϖ electrons in the polyyne unit in bdi[4-], which is evidently stronger than that for the phenyl rings in other ligands in the NbO-type MOFs. In addition, the replacement of phenyl rings by polyyne chain leads to a boost of pore volume and hydrogen uptake. Furthermore, in the absence of a catalyst, the hydrogen addition reaction on the polyyne unit has not been observed even at high pressure as shown by the reversible hydrogen sorption isotherms of PCN-46, validating the stability of the MOF under hydrogen storage conditions.

(c) An Isoreticular Series of MOFs with Dendritic Hexa-Carboxylate Ligands and Exceptionally High H_2 Uptake Capacity

It has been well established that the high-pressure gravimetric hydrogen adsorption capacity of a MOF is directly proportional to its surface area. However,
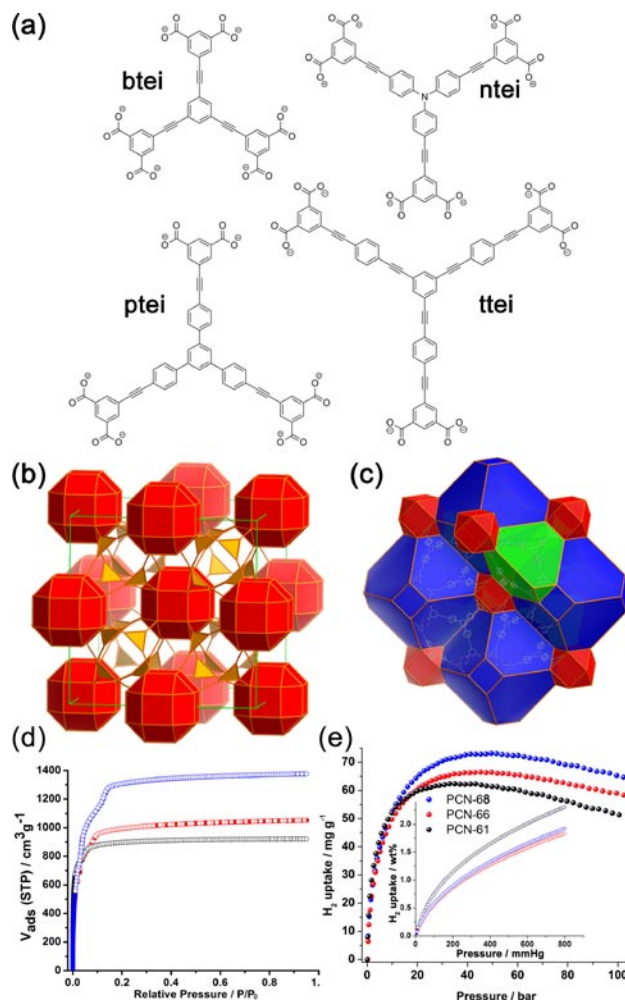

FIGURE 3. (a) Nanoscopic ligands btei (PCN-61), ntei (PCN-66), ptei (PCN-68) and ttei (PCN-610). (b) (3,24)-Connected network in PCN-68. (c) 3D polyhedra packing in PCN-68. (d) N_2 sorption isotherms of PCN-61, PCN-66, and PCN-68 at 77 K. (e) Gravimetric H_2 uptakes in PCN-6X series at 77 K.

MOFs of high surface areas tend to decompose upon activation. In previous work, we've described an approach toward stable MOFs with high surface areas by incorporating mesocavities with microwindows. To extend this work, herein we present an isoreticular series of (3,24)-connected MOFs made from dendritic hexa-carboxylate ligands (Figure 3). In order to test the framework stability, nitrogen sorption measurements were carried out in fully activated PCN-68 and PCN-610. In PCN-68, a dramatic increase of nitrogen sorption has been observed (Figure 3d). The BET surface area calculated based on the low-pressure region data can reach as high as 5,109 m^2 g^{-1}, with a Langmuir surface area of 6,033 m^2 g^{-1}. To the best of our knowledge, PCN-68 possesses the highest surface area reported to date for MOFs based on paddlewheel clusters.

The hydrogen uptake capacities of PCN-6X series are shown in Figure 3e. At a low-pressure region (<1 bar), the hydrogen uptake capacity is mainly controlled by the hydrogen affinity towards the framework, which can be quantified by the isosteric heat of adsorption. PCN-61, which has the smallest pore size, also has the highest heat of adsorption and highest capacity (2.25 wt% at 77 K, 1 bar). PCN-66 and PCN-68 have heats of adsorption and adsorption capacities similar to each other (1.79 wt% in PCN-66 *vs.* 1.87 wt% in PCN-68). This trend is consistent with the nature of physisorption, in which narrower pores would have stronger interactions with guest gas molecules due to increased interaction between the guests and the opposite potential walls within small pores. Unlike low-pressure hydrogen sorption capacity, which is dominated by hydrogen affinity, the maximum excess hydrogen uptake capacity in MOFs, which typically can only be reached at high pressure range, is controlled mainly by the surface area and pore volume. This is consistent with observations in the PCN-6X series. As can be seen from Figure 3e, PCN-68, which has the highest surface area, also has the highest maximum excess hydrogen uptake capacity (7.2 wt%, Table 2), which makes it one of the best adsorbents with the highest gravimetric hydrogen uptake capacity. It is worth noting that the maximum adsorption pressure increases from PCN-61 (33 bar) to PCN-66 (45 bar) and PCN-68 (50 bar), indicating higher pressure is needed to reach maximum adsorption in sorbents with higher pore volumes.

Using the crystal density data, volumetric hydrogen uptake capacities were also calculated. Unlike the trend in gravimetric capacity, where material with the highest surface area has the highest capacity, volumetric capacity follows the opposite trend, which is dominated by the densities of the sorbents. The gravimetric capacity has been emphasized in the past hydrogen storage research, and rightfully so. However, volumetric capacity is particularly relevant in volume-limited fuel cell applications. Both of these criteria should be emphasized equally in the search for ideal hydrogen storage materials.

(d) POFs

In the last decade, the chemistry of porous materials has witnessed a renaissance in design and synthesis of porous polymers. Compared to MOFs, porous polymers have higher chemical and thermal stability, which is suitable for further decoration. Three POFs have been synthesized by homocoupling reactions (Figure 4). The polymeric frameworks have high stabilities and surface areas of up to 5,323 $m^2 g^{-1}$. Their hydrogen uptake capacity at 1 bar is directly proportional to the surface area. This trend is more obvious at higher pressure ranges, with the highest uptake capacity obtained for POF-3 (4.28 wt%, 42 bar), which compares favorably
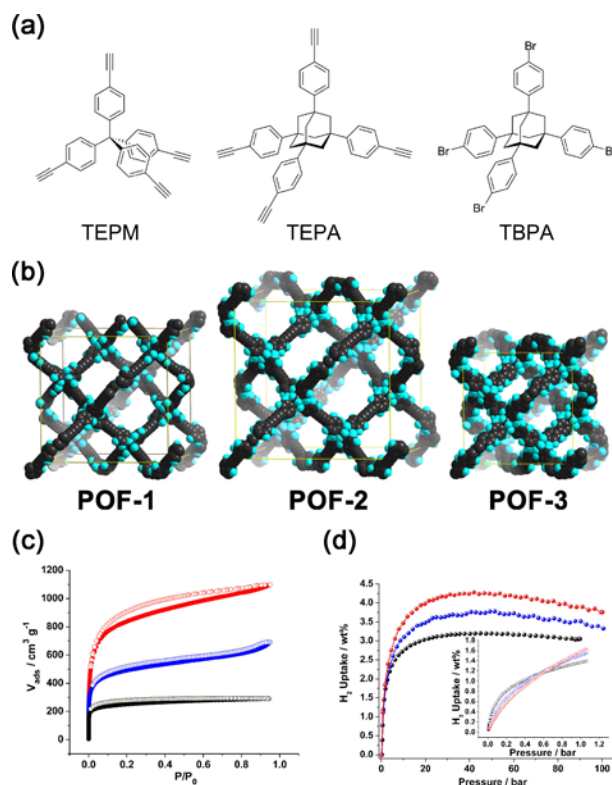

FIGURE 4. (a) Tetrahedral monomers. (b) The default diamondoid frameworks of the POFs generated by coupling reactions (TEPM: POF-1; TEPA: POF-2; TBPA: POF-3). (c) The 77 K N_2 sorption isotherms (black: POF-1; blue: POF-2; red: POF-3). (d) The gravimetric H_2 uptake in POFs at 77 K (black: POF-1; blue: POF-2; red: POF-3).

with the highest ones of carbon materials. This trend is the same for other adsorbents, indicating the importance of a high surface area for maximal hydrogen uptake capacity. Based on a variant of the Clausius-Clapeyron equation, the hydrogen isosteric heat of adsorption can be calculated. Compared with POF-2 and POF-3, the heat of adsorption in POF-1 is surprisingly high (7.59 kJ mol^{-1}) and, most importantly, it remains almost constant over the whole gas loading range. This value is higher than those for other porous polymer analogs, such as PAF-1 (4.6 kJ mol^{-1}) and covalent-organic frameworks (6.0-7.0 kJ mol^{-1}). The high heat of adsorption may stem from the narrower pores, which allow stronger overall interactions of the guest gas molecules because of additional interactions with the opposite walls. In addition, the polyyne motifs may help to increase the gas affinity as well. This hydrogen affinity difference is reflected in the hydrogen sorption isotherms at a lower pressure range (less than 0.5 bar), where the hydrogen uptake in POF-1 rises most steeply. In the higher pressure range, where the surface area and pore volume become dominant, POF-3 has the highest uptake capacity.

Conclusions and Future Directions

Conclusions:

- α Phase NbO-type copper MOFs should be better for gas storage than their β phase counterparts.
- Small pores (5 to 10 Å) in MOFs lead to an increased effective surface area, offering more adsorption sites for hydrogen.
- The polyyne chains showed improved hydrogen affinity compared to phenyl rings.
- Constructing MOFs containing mesocavities with microwindows is proven as a general approach towards stable MOFs with high surface areas and high hydrogen uptake.
- Porous organic frameworks with tunable pore size and surface area can be prepared with high chemical and thermal stability, which are good candidate for hydrogen storage.

Future Directions:

- Further enhancement of H_2-MOF interaction by doping coordinatively unsaturated metal centers (heat of adsorption 15 kJ/mol). Based on theoretical calculations, main group metals such as Mg and Ca will be tested.
- Working with partners, test H_2 uptake at temperatures higher than 77 K.
- Preparation of MOFs with high surface area and optimized cage size with newly designed ligands based on theoretical calculations.
- Incorporation of entatic-state metals based on theoretical guidance.
- Preparation of POFs containing active metals.

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