Further Investigation of the Effect of Framework Catenation on Hydrogen Uptake in Metal−Organic Frameworks

Shengqian Ma,[†,#] Juergen Eckert,[‡] Paul M. Forster,*,[§] Ji Woong Yoon,[||]
Young Kyu Hwang,[||] Jong-San Chang,*,[||] Christopher D. Collier,[†] John B. Parise,[⊥]
and Hong-Cai Zhou*,[†]

*Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas
77842-3012, Materials Research Laboratory, University of California, Santa Barbara, California
93106, Department of Chemistry, University of Nevada, Las Vegas, Nevada 89154, Catalysis
Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT),
Jang-dong 100, Yuseong-Gu, Daejon 305-600, Korea, and Mineral Physics Institute, Stony
Brook University, Stony Brook, New York 11794*

Received May 10, 2008; E-mail: zhou@mail.chem.tamu.edu; Paul.Forster@unlv.edu; jschang@krict.re.kr

Abstract: Hydrogen-sorption studies have been carried out for the catenation isomer pairs of PCN-6 and PCN-6′ (both have the formula of $Cu_3(TATB)_2$, where TATB represents 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoate with a formula of $C_{24}H_{12}N_3O_6$). Inelastic neutron scattering (INS) studies reveal that the initial sites occupied by adsorbed H_2 are the open Cu centers of the paddlewheel units with comparable interaction energies in the two isomers. At high H_2 loadings, where the H_2 molecules adsorb mainly on or around the organic linkers, the interaction is found to be substantially stronger in catenated PCN-6 than in noncatenated PCN-6′, leading to much higher H_2 uptake in the isomer with catenation. Hydrogen sorption measurements at pressures up to 50 bar demonstrate that framework catenation can be favorable for the enhancement of hydrogen adsorption. For example, the excess hydrogen uptake of 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, respectively, and that for 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 a total volumetric value of 53.0 g/L, estimated based on crystallographic density) at 77 K/50 bar and 15 mg/g (1.5 wt %) at 298 K/50 bar. Significantly, the expected usable capacity of PCN-6 is as high as 75 mg/g (or 41.9 g/L) at 77 K, if a recharging pressure of 1.5 bar is assumed.

Introduction

The lack of a safe and efficient on-board hydrogen storage method has been recognized as a major hurdle preventing the widespread use of hydrogen for mobile applications.[1] Among a variety of hydrogen storage candidates,[2] porous metal−organic

frameworks (MOFs)[3] remain one of the most studied new materials applied to approach the DOE on-board storage targets,[1] because of their high specific surface areas[4] and well-defined

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† Texas A&M University.
‡ University of California, Santa Barbara.
§ University of Nevada, Las Vegas.
|| KRICT.
⊥ Stony Brook University.
Current address: Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439.

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hydrogen-framework-interacting sites.[5] Some of the MOFs have arguably reached or even surpassed the DOE 2010 hydrogen storage target, albeit at cryogenic temperatures (mostly at 77 K), and the DOE goals are "system targets", taking into consideration the weight of the storage tank and other essential parts.[6] To improve the hydrogen uptake of porous MOFs, particularly at near ambient temperatures, various strategies such as increasing surface areas,[3j] using small pore sizes comparable to hydrogen molecules,[7] introducing accessible open-metal sites,[6b,c,8] implementing naked alkali metal cations,[9] and utilizing catenation[10] have recently been widely explored.

Catenation, the intergrowth of two or more identical frameworks, has long been an interesting topic in MOF research.[11] 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.[12] Some catenated porous MOFs have been reported to adsorb ~1 wt % of hydrogen at room temperature and 48 bar.[13]

Recently, we developed a templating strategy to control catenation/noncatenation in porous MOFs effectively and were able to quantitatively evaluate the contribution from catenation to the hydrogen uptake of a MOF material (Figure 1).[14] Our studies revealed that catenation can lead to a 41% improvement of *apparent* Langmuir surface area (3800 m^2/g for PCN-6 vs 2700 m^2/g for PCN-6′), a 29% increase in excess gravimetric hydrogen uptake at 77 K/760 torr, and a 133% increase in volumetric hydrogen uptake in the catenation isomer pair of PCN-6/PCN-6′ (both have the formula of Cu$_3$(TATB)$_2$, where TATB represents 4,4′,4″-s-triazine-2,4,6-triyl-tribenzoate with a formula of C$_{24}$H$_{12}$N$_3$O$_6$). Similar observations were also reported by Long and co-workers in the ligand-directed catena-
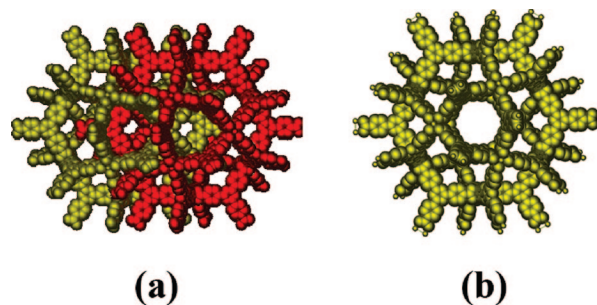
Figure 1. (a) Catenated PCN-6. (b) Noncatenated PCN-6′.

tion studies.[15] However, due to the possibility that catenation may ultimately lead to a nonporous material, suspicions arose on whether or not catenation will lead to improved hydrogen uptake at near saturation conditions. It is thus imperative to find the mechanistic details of the interaction between hydrogen molecules and catenated frameworks.

It has been well-documented that hydrogen adsorption in porous MOFs is closely related to their structural features,[12] and it is therefore essential that the interactions between hydrogen molecules and binding sites in these frameworks be elucidated.[3h] The most useful experimental method for obtaining a molecular level understanding of hydrogen adsorption in porous MOFs is inelastic neutron scattering (INS) spectroscopy of the hindered rotational transitions of the adsorbed hydrogen molecules.[16] The lowest transition hindered rotor energy level of the H$_2$ molecule is a rotational tunneling transition, which depends exponentially on the height of the barrier to rotation. It is for this reason that this technique is extremely sensitive to the chemical environment of adsorbed H$_2$ and can thereby provide detailed information about the various binding sites that the hydrogen molecules occupy and the approximate order in which these are filled.[17] Because of the very large inelastic incoherent neutron scattering cross section for hydrogen, vibrational modes not involving hydrogen are not normally observed, which greatly simplifies the analysis of the observed spectra. This technique has become invaluable to the understanding of the hydrogen adsorption characteristics of a variety of nanoporous substrates including zeolites[18] and carbon nanostructures[19] and has also been recently employed to investigate the details of hydrogen adsorption in porous MOFs.[8c,20]

To clarify how catenation improves hydrogen uptake, and to elucidate the different hydrogen adsorption mechanisms in the catenated and noncatenated frameworks, herein we report the INS investigation of hydrogen adsorption in the catenation isomer pairs of PCN-6 and PCN-6′, the analysis of their heats

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of hydrogen adsorption, and hydrogen-sorption studies under pressures up to 50 bar.

Experimental Section

Sample Preparation. PCN-6 and PCN-6′ were synthesized by following the methods described previously.[14] The prepared fresh samples were immersed first in methanol and then dichloromethane to exchange the included DMSO or DMF solvent molecules. After solvent exchange, the samples were evacuated at room temperature overnight and activated under a dynamic vacuum at 150 °C for 2 h. The crystalline phase purity of each activated sample was confirmed by comparing the powder X-ray diffraction patterns (collected on a Scintag X1 powder diffractometer system using Cu K radiation with a variable divergent slit, solid-state detector, and a routine power of 1400 W/40 kV/35 mA) with those simulated from single crystal data (Figure S1). For comparison of H_2 uptakes, Cu-BTC (also known as HKUST-1 in a previous report[4c]) was prepared using microwave-assisted hydrothermal synthesis using H_3BTC (benzene-1,3,5-tricarboxylic acid, 2 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (3.65 mmol) at 140 °C for 1 h (see Supporting Information).

Inelastic Neutron Scattering Experiments. Inelastic neutron scattering spectra were collected on the QENS spectrometer at the Intense Pulsed Neutron Source at Argonne National Laboratory. The samples of PCN-6 and PCN-6′ were dehydrated for 2 h in a tube furnace set to 423 K. A quantity of 1.0 g of each material was subsequently individually sealed inside an aluminum sample container in a solvent-free N_2 glovebox. The container was then mounted in a closed-cycle He refrigerator, connected to an external gas loading manifold, and placed into the QENS instrument. After degassing for 1 h, the sample was cooled to 15 K and a "blank" spectrum of the material was collected for ~12 h. Gas loadings were carried out in situ with the sample container at 70−150 K by monitoring the pressure drop from the calibrated volume of the manifold of the external gas handling system. Each of a total of three loadings delivered 4.2×10^{-2} mol of H_2 gas to the sample.

Low-Pressure Hydrogen Adsorption Measurements. The low-pressure hydrogen adsorption isotherms in the range 0−800 torr were measured using a Beckman Coulter SA 3100 surface area and pore size analyzer. High purity hydrogen (99.9995%) was used for H_2 adsorption measurements. The regulator and pipe were flushed with hydrogen before connecting to the analyzer. The internal lines of the instrument were flushed three times utilizing the "flushing lines" function of the program to ensure the purity of H_2. Before the measurement, the activated samples were again evacuated by heating at 150 °C under a dynamic vacuum ($<10^{-3}$ torr) for 2 h by using the "outgas" function of the surface area analyzer. The evacuated sample tube containing degassed samples was covered with a rubber cap and then carefully transferred to an analytical balance (0.0001 mg accuracy) and weighed to determine the mass of the sample (typically 60−150 mg). The tube was then transferred back to the analysis port of the surface area analyzer and evacuated to a vacuum of less than 10^{-3} torr before the first gas dose. For all the isotherms, the free-space corrections were performed using high-purity He gas (99.999%). The H_2 adsorption isotherms at 77 K were measured in a liquid nitrogen bath, and those at 87 K were measured in a liquid argon bath.

High Pressure Gas Adsorption Measurements. The high pressure adsorption experiments were conducted using a volumetric sorption analyzer HPVA-100 (VTI Corporation, USA) equipped with a rotary vane pump (DUO 5 M, PFEIFFER), a turbomolecular drag pump (TMH 064/TMU 064, Pfeiffer), a PMP 4010 (Druck/GE, Max. Six MPa) transducer, a Datel pressure meter, a JC Controls TC610 vacuum gauge, and a Polyscience circulator. The sample holder consisted of a sample cell and tube equipped with a diaphragm valve (6LV-DSBW4, Swagelok). The two assemblies were connected via a filter gasket (SS-4-VCR-2-.5M, Swagelok), and the materials of construction were all 316 stainless steel. The volumetric technique consisted of dosing a known amount of gas into the cell containing the sample to be analyzed. When the sample

reached equilibrium with the gas adsorbate, the initial and final equilibrium pressures were recorded. These data were then used to calculate the volume of gas adsorbed by the sample. This process was repeated at given pressure intervals until the maximum preselected pressure was reached. Each of the resulting equilibrium points (volume adsorbed and equilibrium pressure) were then plotted to provide an isotherm. Good reproducibility and accuracy were obtained by using separate transducers for dosing the sample and for monitoring the pressure in the sample cell. In a typical experiment, at least 0.25 g of sample was transferred to the sample cell and outgassing was performed overnight at 423 K under high vacuum (~0.001 Pa). After finishing the outgassing, the sample cell was recharged with He (99.999%) to measure the loading amounts of the dehydrated samples, which were calculated from the weight difference between the blank sample cell and sample-loaded cell. The above activation was repeated again, and then a gas sorption experiment was performed. Ultrahigh purity H_2 (99.999%) was obtained from Korea Gas Co. The sample cell was immersed in a thermostatted circulating bath at 303 K.

The total hydrogen uptake defined as the total amount of hydrogen stored in the bulk volume of the materials can usually provide another informative quantity. The total H_2 adsorption was calculated by using the method reported for other MOFs.[6b,g] The total adsorption capacity is expressed as follows:

$$C_{tot} = C_{exc} + (100 \times d_g \cdot V_{pore})/(1 + d_g \cdot V_{pore})$$

where C_{tot} is the total adsorption capacity expressed in weight percent (wt %), C_{exc} is the excess adsorption in wt % which is the quantity being measured, d_g is the density of the compressed H_2 gas at a tested temperature and pressure in g/cm³, and V_{pore} is the pore volume, cm³/g. The pore volumes, 1.453 cm³/g for PCN-6 and 1.045 cm³/g PCN-6′, respectively, were measured experimentally from N_2 adsorption isotherms at $P/P_0 = 0.99$ and $T = 77$ K.

Results and Discussion

Analysis of Isosteric Heats of Adsorption. It is believed that the reduced pore size resulting from catenation increases the overlap of the attractive potential of opposite walls thus enhancing the heat of adsorption.[3e,21] To estimate the heats of adsorption (Q_{st}) for H_2 in PCN-6 and PCN-6′, H_2 adsorption isotherms were measured at 77 and 87 K (Figure S2). The adsorption data were fitted using the Langmuir−Freundlich equation[22] (utilizing the virial-type expression[3e,6b] to fit the data could yield similar results but with large (~15%) deviations), and the heats of adsorption were calculated using the Clausius−Clapeyron equation:[23]

$$Q_{st} = -R * d(\ln P)/d(1/T)$$

As shown in Figure 2, in the uptake range 0.05−7 mmol/g, the Q_{st} of PCN-6 is 6.2−4.5 kJ/mol, while that of PCN-6′ is 6.0−3.9 kJ/mol. At a low coverage of 0.05 mmol/g, PCN-6 has a hydrogen-adsorption enthalpy of 6.2 kJ/mol and that for PCN-6′ is 6.0 kJ/mol. These are comparable to the reported Q_{st} of Cu-BTC[3e,24] and can be attributed to the interactions between dihydrogen molecules and open Cu sites as revealed by the recent neutron powder diffraction studies.[5b] With the increase of H_2 coverage, the Q_{st} of the two MOFs decreases steadily but drops more rapidly in PCN-6′. The larger Q_{st} of PCN-6

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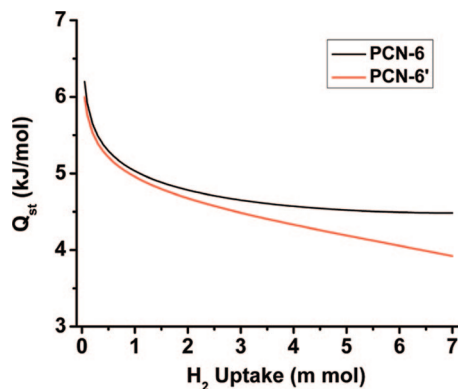
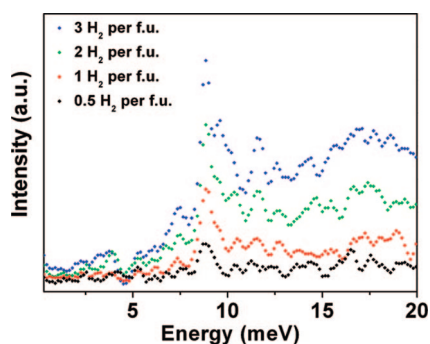**Figure 2.** Isosteric heats of adsorption for PCN-6 and PCN-6′.

Figure 3. INS spectra (15 K) for H_2 adsorbed in PCN-6 at loadings of 0.5, 1, 2, and 3 molecules per Cu site.

compared to that of PCN-6′ at high H_2 coverage can be ascribed to the reduced pore size of PCN-6 due to catenation thereby enhancing the interaction energy between dihydrogen molecules and the framework walls.[12,21]

Inelastic Neutron Scattering (INS) Studies. INS spectra were obtained from a sample of 1.0 g of PCN-6 and of PCN-6′ on the QENS spectrometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. Each sample was evacuated at temperatures up to 150 °C and transferred under a He atmosphere into the sample holder for the neutron scattering experiments. Following the collection of a data set of the "blank" sample at 15 K, the sample was warmed to 77 K, and an amount of hydrogen corresponding to 0.5 molecule per Cu was adsorbed in situ. Subsequent data sets with two or three additional loadings (also at 77 K) of hydrogen were obtained at 15 K. The INS spectra for H_2 in PCN-6 and PCN-6′, after subtracting the "blank" run, are shown in Figures 3 and 4. The identifiable peaks in the INS spectra were assigned based on the same model previously used by us,[20a] namely that of a hindered rotor with two angular degrees of freedom in a simple double-minimum potential.[25] In the absence of a barrier to rotation, the lowest transition is that between *para-* and *ortho*-H_2 and it occurs at 14.7 meV (or 119 cm^{-1} = $2B$, where B is the rotational constant of the H_2 molecule). The interaction of the adsorbed hydrogen molecules with the host material gives rise to a barrier to rotation which in turn partially lifts the degeneracy of the $J = 1$ level. The lowest transition frequency for the hindered rotor (between the $J = 0$ and the $J = 1$, $m_J = 0$ states, which we subsequently refer to as the "0−1" transition) decreases approximately exponentially with increasing barrier height (rotational tunnel
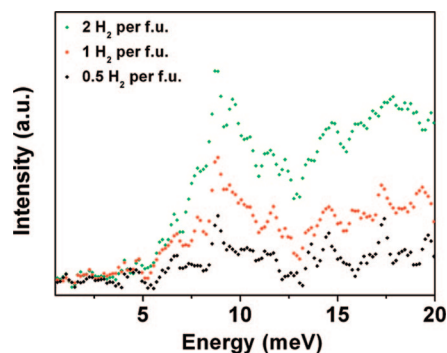
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Figure 4. INS spectra (15 K) for H_2 adsorbed in PCN-6′ at loadings of 0.5, 1, and 2 molecules per Cu site.

Table 1. Tentative Assignments of Bands in the INS Spectra of PCN-6 and PCN-6′ According to the Model Used in Ref 20a[a]

material	loading (H_2 per Cu)	transition energy (meV)			barrier height (kJ/mol)
		0−1	0−2	1−2	
PCN-6		8.7	19.1	10.4	2.485
	0.5	9.5	18.3	8.8	2.059
		11.3	16.7	5.4	1.278
		11.6	16.6	5.0	1.207
	1	12.9	15.7	2.8	0.639
		10.3	17.7	7.4	1.739
	2	14.0	15.0	(1.0)	0.248
PCN-6′		8.85	19.0	10.2	2.414
	0.5	11.6	16.6	5.0	1.207
		13.7	15.2	(1.5)	0.355
		14.5	14.8	(0.3)	0.071
	1	9.6	18.3	8.8	2.059
		10.2	17.8	7.6	1.775

[a] 1 meV = 8.07 cm^{-1}.

splitting) and is therefore extraordinarily sensitive to small differences in barrier height (see Table 1). All rotational energy levels are labeled sequentially for reasons of simplicity, i.e., 0, 1, 2, and not by quantum numbers. Peak positions are approximate; some of the 1−2 transitions (in parentheses) were not observed most likely because of low population of the "1" level.

Previous studies[5b,20c] of porous MOFs containing the Cu paddlewheel SBU have shown that the preferred binding site for H_2 is the open Cu site, and this is also found to be the case in PCN-6/PCN-6′. The lowest loading used in the INS studies in both cases was 0.5 H_2 per Cu site with the assumption that only this site would be occupied. The INS spectra at this low loading indeed show mainly one prominent peak at ~8.8 meV in both compounds, which we can readily assign to H_2 adsorbed at the open Cu sites. We note, however, that the peak for H_2 in PCN-6 is somewhat broader than that in PCN-6′. This difference can be ascribed to the fact that in PCN-6 there are three inequivalent Cu sites whereas all those sites in PCN-6′ are identical. One may speculate that the catenation in PCN-6 may at least in part give rise to slight differences in the coordination geometry about the three Cu sites, which in turn affect binding of H_2 as well as that of the water ligand initially present. A rough assessment of the differences in Cu...H_2 interaction strengths at these sites can be obtained by comparing the Cu−OH_2 distances found for the removable aqua ligands of the paddlewheel SBUs in the crystal structures. In PCN-6[10a] there are three such Cu−O distances of 2.199, 2.110, and 2.140 Å (average 2.150 Å) whereas the one such distance in PCN-6′ is 2.173 Å.[14] If we can assume that those for Cu...H_2 would be

Table 2. Hydrogen Uptake Data of PCN-6 and PCN-6′ under 50 Bar

	enthalpy (kJ/mol)	excess (77 K) mg/g	excess (77 K) g/L	total (77 K) mg/g	total (77 K) g/L	deliverable (77 K/1.5−50 bar)	excess (298 K) mg/g	total (298 K) mg/g
PCN-6	6.2−4.5	72	40.2	95	53.0	75 mg/g (41.9 g/L)	9.3	15
PCN-6′	6.0−3.9	42	11.8	58	16.2	42 mg/g (11.8 g/L)	4.0	8.1

proportional to these distances, we might conclude that the average interaction with the Cu sites in PCN-6 is slightly greater than that in PCN-6′.

Close inspection of the band in the INS spectrum corresponding to the 0−1 transition in both systems does indeed reveal that the position of this peak is at slightly lower energy (8.7 meV) in PCN-6 (indicating stronger interaction with H_2) than in PCN-6′ (8.85 meV). This observation is qualitatively in agreement with the relative Q_{st} values of 6.2 kJ/mol for PCN-6 vs 6.0 kJ/mol for PCN-6′ at low coverage. It must, however, be noted that the barrier to rotation for H_2 as determined from the INS experiment does not necessarily have a one-to-one correspondence with the binding energy.[26] Nonetheless previous studies[20a] have shown that in general a larger barrier for rotation of H_2 at a particular site is associated with a higher binding energy. The greater width of this peak for H_2 in PCN-6 may also reflect the presence of three different Cu sites, which slightly differ in binding energies for H_2.

The general appearance of the INS spectra for both compounds is rather similar, which does of course reflect the identical chemical composition. Some important differences are evident, however, as a result of the framework catenation in PCN-6. The presence of interpenetrating frameworks in PCN-6 should make it possible for the adsorbed H_2 to interact with more atoms than in PCN-6′ because of the proximity of the "second" framework and, hence, result in some increase in binding energies. Inspection of the crystal structures of the two compounds shows that this effect is likely to be more pronounced for sites on or near the organic linkers than those on or near the open Cu sites.

The rotational transition energies associated with H_2 on the organic linkers tend to be in the region between 11 and 14.7 meV.[20] The latter is the value of the 0−1 transition for the free rotor. All the INS intensities above that value originate from higher transitions. Comparison of the INS spectra in this energy range at higher loadings in PCN-6′ show a strong peak growing in at ~14.5 meV, which is rather weak in PCN-6. Instead, the spectrum for PCN-6 shows that a peak at 11.6 meV develops and increases with higher loadings. The transition at about 14.5 meV is well-known from work on H_2 adsorbed on various carbons[27] as well as on organic links in MOFs[20a] and reflects the rather weak binding to those structures. The apparent shift to much lower energy (i.e., stronger interaction) demonstrates that the binding sites on the linkers in PCN-6 are strongly affected by catenation, and this observation is indeed reflected by the higher values for Q_{st} for PCN-6 at higher loadings.

An interesting observation related to H_2-binding sites on the organic linkers may be also made from the H_2-loading depen-
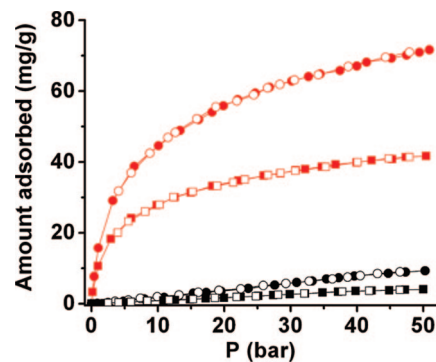
Figure 5. Excess hydrogen sorption isotherms of PCN-6 and PCN-6′ at 77 (red) and 298 K (black): circles, PCN-6; squares, PCN-6′; solid symbols, adsorption; open symbols, desorption.

dence of the strong peak at 4.5 meV which arises from the framework. This peak may be assigned to the torsion of the benzene carboxylate, and this motion has in fact been studied by NMR for benzene dicarboxylate in MOF-5.[28] It occurs at a similar energy in the INS of the MOF-5 framework.[20a] This peak has been subtracted out in the spectra shown in Figures 3 and 4, but the difference spectrum shows much more intensity in the region ~4.5 meV at higher H_2-loading for PCN-6 than PCN-6′. This increase results from H_2 molecules bound to sites on the benzene carboxylate and hence participating in the torsional motion along with the H's from the organic ligand.

The INS studies therefore clearly indicate that the much stronger interactions of adsorbed H_2 with the organic linker in the catenated material must result from a greater number of interacting atoms from the organic ligands, especially at high hydrogen loadings. These results are also consistent with recent theoretical simulations suggesting that catenation favors hydrogen uptake by maximizing the *effective* hydrogen binding sites on the organic linkers.[29]

High-Pressure H_2 Sorption Studies. To check the hydrogen sorption behaviors of the isomer pairs at elevated pressure, H_2 sorption isotherms under up to 50 bar of pressure were measured at 77 and 298 K. As shown in Figure 5, at 77 K/50 bar, the excess H_2 uptake of PCN-6 can reach as high as 72 mg/g (or (72/(1000 + 72) = 6.7 wt %) without reaching saturation. This value, to the best of our knowledge, is among the highest for reported porous MOFs under 77 K/50 bar (for MOF-177, the uptake is 71 mg/g at 50 bar and 75 mg/g at 70 bar,[6a,f] Table 3), and it is expected to increase further at higher pressure before the saturation is reached (fitting the adsorption isotherm with Langmuir−Freundlich equation, an excess saturation hydrogen uptake of 89 mg/g can be expected). Calculated based on the crystallographic density of 0.558 g/cm³ after removal of the axial aqua ligands from the Cu atoms, the excess volumetric H_2 uptake of PCN-6 is 40.2 g/L. At 298 K and 50 bar, PCN-6 can adsorb 9.3 mg/g (0.92 wt %) hydrogen, among the best for reported porous MOFs.[3j,o,7,13] As for PCN-6′, its excess H_2 adsorption is 42 mg/g (4.0 wt %) at 50 bar without reaching saturation, corresponding to an excess volumetric value of 11.8 g/L (using a crystallographic density of 0.280 g/cm³). At 298

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Table 3. Hydrogen Adsorption Data of PCN-6 and Some Reported MOFs

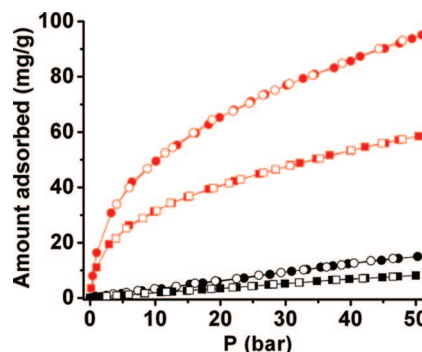|	excess, wt % 77 K	excess, g/L 77 K	total, wt % 77 K	total, g/L 77 K	excess, wt % 298 K	total, wt % 298 K
PCN-6	6.7 (50 bar)	42.3 (50 bar)	8.7 (50 bar)	53.0 (50 bar)	0.92 (50 bar)	1.5 (50 bar)
MOF-177[6g]	7.0 (70 bar)[a]	32.0 (70 bar)[a]	9.9 (70 bar)	48.3 (70 bar)	0.68 (100 bar)[31]	
Mn-BTT[6b]	5.1 (35 bar)[a]	44.3 (35 bar)[a]	6.9 (90 bar)	60 (90 bar)	~0.8 (90bar)	1.4 (90 bar)
Cu-BTT[6c]	4.2 (30 bar)[a]	38.0 (30 bar)[a]	5.7 (90 bar)	53 (90 bar)	~0.4 (90 bar)	
MIL-101[e]	6.1 (80 bar)				0.43 (80 bar)	
MOF-5[3h]	5.1 (60 bar)[a]				0.28 (60 bar)	
MOF-5[6g]	7.1 (40 bar)[a]	46.9 (40 bar)[a]	10.0 (100 bar)	66.0 (100 bar)		
Cu2(tptc)[6d]	6.06 (20 bar)	43.6 (20 bar)				
Cu2(qptc)[6d]	6.07 (20 bar)	41.1 (20 bar)				
PCN-11[32]	5.04 (45 bar)[a]	37.8 (45 bar)[a]	5.97 (45 bar)	44.7 (45 bar)		
UMCM-150[3m]	5.7 (45 bar)[a]	36.0 (45bar)				

[a] Saturation uptake.

K and 50 bar, PCN-6′ can adsorb 4.0 mg/g (0.40 wt %) hydrogen, which is less than half of the amount PCN-6 adsorbs.

Since PCN-6′ is isostructural with the well-studied Cu-BTC, high-pressure H₂-sorption data were also collected to calibrate the high-pressure adsorption studies in this work. The excess hydrogen uptake of Cu-BTC is 3.4 wt % (Figure S5, the isotherm reaches saturation at 77 K and 20 bar) and 0.34 wt % at 298 K, 50 bar, consistent with the results reported by others.[3h] The higher hydrogen uptake of PCN-6′ at high pressure compared to that of Cu-BTC can be ascribed to the larger surface area of PCN-6′.[29c,30]

On the other hand, the higher hydrogen uptake of PCN-6 compared to that of PCN-6′ can be attributed to not only the increased surface area but also the reduced pore size (9.0 Å) as a result of catenation. Catenation can increase the overlap of the attractive potential of opposite walls thus enhancing the interaction between hydrogen molecules and the frameworks,[21] and the boosted energy fields of the pore walls also increase the number of *effective* hydrogen binding sites.[29] As for PCN-6′, although it has a larger solvent-accessible volume, the long distance (21.4 Å) between the opposite pore walls leads to virtually no overlap of the potential energy fields. Such an open structure results in unused space at the center of the pores and a decrease of the number of *effective* hydrogen binding sites. This is consistent with the preceding INS studies and is reflected in the higher adsorption enthalpy of PCN-6.

For practical applications, the total hydrogen uptake, defined as the total amount of hydrogen stored in the bulk volume of the materials, can usually provide another informative quantity. The total H₂-adsorption capacity of PCN-6, as shown in Figure 6, can reach 95 mg/g (8.7 wt %) at 77 K/50 bar, corresponding to a volumetric uptake of 53.0 g/L; both are record highs among those reported in porous MOFs (Table 3) under 77 K/50 bar (~8.0 wt % or 52.8 g/L under the same condition for MOF-5 reported in ref 6g). At these conditions, the total hydrogen uptake of PCN-6′ is 58 mg/g (5.5 wt %) corresponding to a volumetric value of 16.2 g/L. At 298 K and 50 bar, the total hydrogen-adsorption capacity of PCN-6 is 15 mg/g (1.5 wt %), while that of PCN-6′ is 8.1 mg/g (0.80 wt %).

Recent studies on total or excess hydrogen uptake at 77 K and applicable pressures have led to the assessment that porous

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Figure 6. Total hydrogen-sorption isotherms of PCN-6 and PCN-6′ at 77 K (red) and 298 K (black): circles, PCN-6; squares, PCN-6′; solid symbols, adsorption; open symbols, desorption.

MOFs are promising cryogenic hydrogen storage media (77 K)[6] to reach the 2010 DOE hydrogen storage targets. However, a more important criterion for on-board hydrogen storage is the total amount of deliverable H₂, which can be defined as the absolute deliverable amount of H₂ assuming that recharge starts at 1.5 bar of pressure.[6f] This means that the hydrogen uptake at 1.5 bar always remains in the storage tank and has no contribution to the deliverable storage capacity. As shown in Figures 5 and 6, hydrogen sorption isotherms of PCN-6 and PCN-6′ are fully reversible with virtually no hysteresis. At 77 K and 50 bar, the total amount of deliverable hydrogen of PCN-6 is 75 mg/g (or 41.9 g/L) and that of PCN-6′ is 42 mg/g (or 11.8 g/L). The deliverable hydrogen capacity of PCN-6 (41.9 g/L between 1.5 and 50 bar) is higher than that of MOF-177, which can deliver 40.0 g/L when the charging and discharging pressures are 1.5 and 70 bar, respectively.[6f]

Conclusions

In summary, the study of isosteric heats of adsorption indicated that catenated PCN-6 and noncatenated PCN-6′ have similar hydrogen-adsorption enthalpies at low coverage. However, as the hydrogen load increases, PCN-6 exhibits steadily higher hydrogen-adsorption enthalpies than those of PCN-6′. INS 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 noncantenated 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 %) 298 K/50 bar. Significantly, the deliverable 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.

Supporting Information Available: PXRD patterns, H_2 adsorption isotherms of PCN-6 and PCN-6′ at pressures up to 1 bar, and H_2 adsorption isotherms of HKUST-1 up to 50 bar. This material is available free of charge via the Internet at http://pubs.acs.org.

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