FINAL TECHNICAL REPORT FOR THE US DEPARTMENT OF ENERGY

Executive Summary

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressure gas or very low temperature liquid. Because of the importance of hydrogen as a fuel, the DOE has set system targets for hydrogen storage of gravimetric (5.5 wt%) and volumetric (40 g L^{-1}) densities to be achieved by 2015. Given that these are system goals, a practical material will need to have higher capacity when the weight of the tank and associated cooling or regeneration system is considered. The size and weight of these components will vary substantially depending on whether the material operates by a chemisorption or physisorption mechanism. In the latter case, metal-organic frameworks (MOFs) have recently been identified as promising adsorbents for hydrogen storage, although little data is available for their sorption behavior.

This grant was focused on the study of MOFs with these specific objectives. (1) To examine the effects of functionalization, catenation, and variation of the metal oxide and organic linkers on the low-pressure hydrogen adsorption properties of MOFs. (2) To develop a strategy for producing MOFs with high surface area and porosity to reduce the dead space and increase the hydrogen storage capacity per unit volume. (3) To functionalize MOFs by post synthetic functionalization with metals to improve the adsorption enthalpy of hydrogen for the room temperature hydrogen storage.

This effort demonstrated the importance of open metal sites to improve the adsorption enthalpy by the systematic study, and this is also the origin of the new strategy, which termed isoreticular functionalization and metalation. However, a large pore volume is still a prerequisite feature. Based on our principle to design highly porous MOFs, guest-free MOFs with ultrahigh porosity have been experimentally synthesized. MOF-210, whose BET surface area is 6240 m^2 g^{-1} (the highest among porous solids), takes up 15 wt% of total H_2 uptake at 80 bar and 77 K. More importantly, the total H_2 uptake by MOF-210 was 2.7 wt% at 80 bar and 298 K, which is the highest number reported for physisorptive materials.

Hydrogen Storage in Metal-Organic Frameworks

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Objectives

- Utilize new concepts for increased surface area
- Implement strategies for higher adsorption energy
- Develop strategies for increased hydrogen density in MOFs

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

This project consists of conducting fundamental studies of MOFs. Insights gained from these studies will be applied toward the design and synthesis of H_2 storage materials that meet the following DOE 2015 H_2 storage targets:

- Volumetric density: 40 g L^{-1}
- Gravimetric density: 5.5 wt%

Accomplishments

- More than 35 new MOFs were prepared (IRMOF-19, 20, 61, 62, 76, 77, MOF-114 to 119, 153, 180, 200, 202, 205, 210, 253, 324 to 326, 505, 601 to 604, IRMOP-50 to 53, MOP-14, 15, 17, 23, 24, 54).
- Effects of functionalization, catenation, and variation of the metal oxide and organic linkers on the low-pressure H_2 adsorption properties of MOFs were studied.
- Collected high-pressure H_2 isotherms for a series of MOFs with various functionalities at 77 K which leads to saturation at pressures between 25 and 80 bar.
- Showed H_2 saturation uptake in MOFs correlates well with surface area.
- From H_2 adsorption results, total H_2 uptakes in the MOF materials were estimated.
- Independent measurements of H_2 uptake in MOF-177 were performed by volumetric and gravimetric methods to verify their saturation H_2 uptake.
- Demonstrated the stability and durability of MOF-177. The measurement confirms that at least 4 wt% of H_2 would be delivered under the present experimental condition (2-60 bar and 77 K).
- By inelastic neutron scattering (INS) spectroscopy, the importance of the organic linking units on the adsorption of H_2 was revealed.
- Developed ring-opening reactions to introduce alkylamine group (-$NHCH_2CH_2NH_2$) for subsequent metalation.
- Environment of the metal coordination sites was studied by the extended X-ray absorption fine structure spectroscopy (EXAFS).
- Applied supercritical CO_2 drying technique for sample activation.

- The highest BET surface area and the largest pore volume among crystalline porous solids was demonstrated.
- 15 and 2.7 wt% H_2 uptake by MOF-210 at 77 and 298 K was achieved.

Introduction

Conventional storage of large amounts of H_2 in its molecular form is difficult and expensive because it requires employing either extremely high pressure as a gas or very low temperature as a liquid. Because of the importance of hydrogen as a fuel, the DOE has set system targets for H_2 storage; the gravimetric (5.5 wt%) and volumetric (40 g L^{-1}) densities to be achieved by 2015. Given that these are system goals, a practical material will need to have higher capacity when the weight of the tank and associated cooling or regeneration system is considered. The size and weight of these components will vary substantially depending on whether the material operates by a chemisorption or physisorption mechanism. In the latter case, metal-organic frameworks (MOFs) have recently been identified as promising adsorbents for H_2 storage [1], although little data are available for their sorption behavior. In this project efforts to overcome the lack of understanding of H_2 physisorption were undertaken. Based on the finding, discovery of highly porous materials with strong affinity for H_2 was endeavored.

Results

An outstanding property of MOFs that has prompted their study as H_2 storage candidates is their large surface areas. Many MOFs have been reported in the literature with surface areas greater than 1000 m^2 g^{-1}, which is higher than that demonstrated for zeolites. In particular, the N_2 isotherm measured for MOF-177 at 77 K exhibited the highest uptake of N_2 for any material in 2004 [2], and gave rise to the BET surface area of 4500 m^2 g^{-1}. The initial study of the H_2 uptake by this material at 77 K revealed that while it did not reach saturation at 1 bar [3], it adsorbed comparatively less than other related materials displaying smaller surface areas. As expected, supercritical H_2 adsorbs more weakly than N_2 at 77 K, and pore-filling is not expected at moderate pressures. Thus, both pore geometry and surface structure must be optimized to increase the uptake in these materials. The study which will be demonstrated in this report is particularly instructive in demonstrating the diversity in MOFs over nanostructured carbon materials, which shows a positive trend in H_2 uptake with surface area.
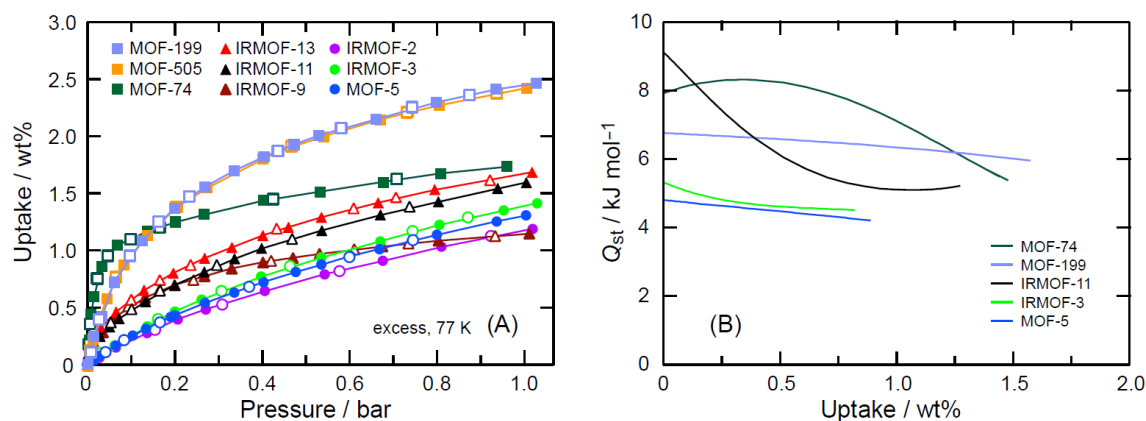
Low pressure hydrogen adsorption in MOFs.
To compare the effects of link functionalization, H_2 isotherms are measured at 77 K for non-catenated MOF-5 (aka isoreticular metal-organic framework-1 (IRMOF-1)), IRMOF-2, and IRMOF-3 (Figure 1) [4]. These results are illustrated in Figure 2. H_2 uptake in IRMOF-3 at 1 bar is slightly higher than that of MOF-5. Therefore, it is likely that amino groups show better interaction with H_2. However, IRMOF-2 shows even lower H_2 uptake than MOF-5 probably due to the large density of the framework. Considering that the incorporated functionality also reduces the pore diameter, which leads to the fact that greater H_2-MOF interaction is expected, the effect of organic functionalites may not be significant enough to realize the drastic improvement of H_2 uptake in the low-pressure region.
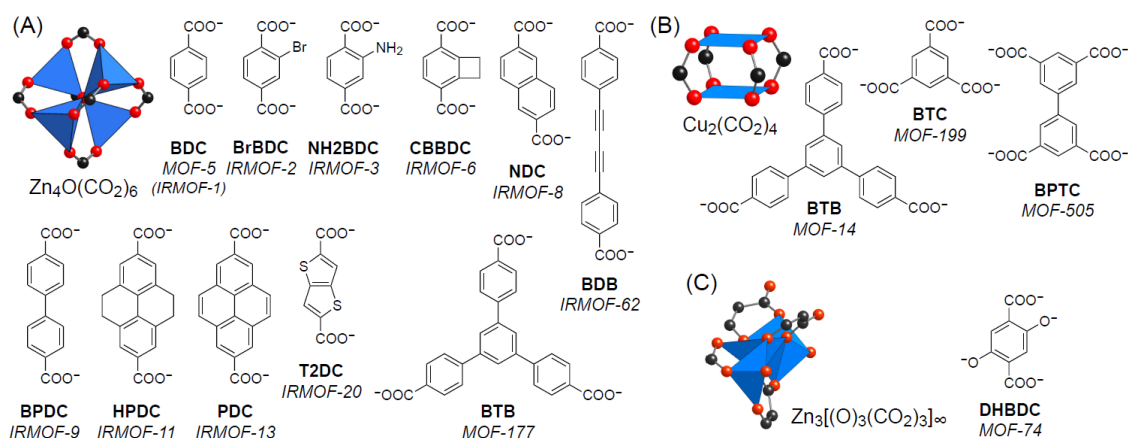
Figure 1. $Zn_4O(CO_2)_6$ (A) and $Cu_4(CO_2)_4$-based (B) MOFs in italics derived from the link in parentheses. (C) MOF-74, based on $\{Zn_3[(O)_3(CO_2)_3]\}_\infty$ 3_1 helices and DHBDC.

For reducing pore dimensions, interpenetration of two or more frameworks should be an effective strategy [4]. The interpenetration may reduce accessible pore volume of materials; especially when a second framework is placed in the middle of the first one. However, it can be said that interwoven structures can keep enough pore volume to store hydrogen molecules, aside from another effect that structural reinforcement may prevent framework collapse. H_2 isotherms for IRMOF-9, 11, and 13 whose catenation numbers are 2, are overlaid in Figure 2. Interpenetrating IRMOF-11 and 13 outperform MOF-5 across the entire range of pressure examined, and IRMOF-9 takes up larger amounts of H_2 below 0.6 bar. When these results are normalized per $Zn_4O(link)_3$ formula unit, the uptakes at 1 bar are nearly double that of MOF-5. Such H_2 uptake behavior at low-pressure region indicates that the adsorption enthalpy for catenated IRMOFs is enhanced because of large Henry's law constant (isotherm slope as P→0).

To improve further both the H_2 uptake capacity and adsorption enthalpy in MOFs, it is necessary to present adsorptive sites with greater interaction potential while maintaining a large total pore volume of appropriate pore dimensions. As expected, MOF-199 and 505 possessing open metal sites (Cu paddle wheel units) show a significant improvement over the other MOFs without them (Figure 2). From the large slopes of isotherms at low pressure region, it is apparent that these materials demonstrate much stronger binding of H_2 due to open Cu^{2+} sites. The amounts adsorbed in gravimetric unit for these MOFs are approximately double that of MOF-5. The isotherm measured for MOF-74 has a particularly large initial slope (Figure 2), which begins to decrease sharply at 0.1 bar. The amount adsorbed at this pressure is 1 wt%, equivalent to 0.8 H_2 per Zn. This feature indicates that H_2 is strongly adsorbed near the open metal sites lining the pore, but as these sites are filled (expected to occur at 1 H_2 per Zn), the increase in uptake with pressure declines as H_2 interacts with weaker secondary sites. This observation provides additional evidence that gains in the low-pressure uptake of H_2 in MOFs can be achieved by stabilizing coordinatively unsaturated centers on their surfaces.

Figure 2. (A) Low-pressure H_2 adsorption isotherms for non-catenated (circles), catenated (triangles) MOFs and MOFs having open metal sites (squares) measured at 77 K. (B) Coverage dependencies of the Q_{st} for H_2 in MOFs.

Isosteric analysis of the heat of adsorption.

In general, when gas molecules are adsorbed on the pore surface, heat is released, indicating that the adsorbed amount should be influenced by the measurement temperature. Therefore, the temperature dependence of H_2 uptake provides useful information regarding H_2-adsorbent interactions. In particular, estimation of the coverage-dependent isosteric heat of adsorption (Q_{st}), which may allow estimation of the number of strong binding sites per unit cell, is a useful diagnosis. For the calculation of the Q_{st} curve, an empirical equation (for instance, the Langmuir–Freundlich model) is applied; however, in most cases, the differential enthalpy derived at low coverage is suspect because the model fits were poor. To estimate reliable Q_{st} of H_2, a virial-type expansion comprising the temperature-independent parameters was used [5,6].

For MOF-5, 74, 199 and IRMOF-3, 11, coverage dependencies of Q_{st} for H_2 were calculated from the fits of their 77 and 87 K isotherms (Figure 2B). As expected, the behavior of the Q_{st} is unique to each MOF. The larger-pore materials (MOF-5, IRMOF-3, and HKUST-1) show a gradual decrease in their values as functions of the amount of H_2 adsorbed. The Q_{st} value for IRMOF-3 is close to MOF-5, indicating that the effect of the NH_2 group is relatively small. On the other hand, the initial Q_{st} value for HKUST-1 is 2.0 kJ mol^{-1} larger than MOF-5, providing further evidence that H_2 interacts more strongly with the $Cu_2(CO_2)_4$ unit than $Zn_4O(CO_2)_6$. No evidence is found for strong binding in the small 6.9 Å secondary pores of MOF-199 under these conditions. In contrast, the Q_{st} for IRMOF-11 drops off considerably from 9.1 to 5.1 kJ mol^{-1} with an increase in the adsorbed amount of H_2. This is indicative of the presence of strong binding sites within the material. Considering that the low Q_{st} values were observed for MOF-5, it is concluded that the stronger interactions in IRMOF-11 should be due to the constrictions in the framework that allow overlap of the attractive potential of proximal surfaces. Finally, MOF-74 displays the largest Q_{st} over much of the range of coverage measured. Interestingly, these values increase with coverage until a maximum of 8.3 kJ mol^{-1} at 0.35 wt% (0.28 H_2 per Zn), inferring that adsorbate-adsorbate interactions are non-negligible at low coverage. Clearly, the small pore dimensions and unsaturated metal sites aid in the low-pressure uptake by this material.

Characterization of H$_2$ Binding Sites in MOFs.

In our first report of H$_2$ storage by MOFs, exceptionally well-defined multiple binding sites for hydrogen within the cavities of MOF-5 were observed by inelastic neutron scattering (INS) spectroscopy with some of these being associated with the organic linking group [1]. These studies to other promising MOFs constructed from Zn$_4$O(CO$_2$)$_6$ units, including IRMOF-8, IRMOF-11, and MOF-177, were expanded to investigate the role of the organic linking group on hydrogen binding (Figure 3A). Despite their chemical similarities, the variation in peak positions associated with sites I (near the metal cluster) and II (near the organic link) of each MOF is significant and clearly indicates that the organic links play an active role in defining the nature of the adsorption sites for H$_2$ (Figure 3B). This is reasonable given the variety of links employed in these materials, which strongly affect the local structure of the Zn$_4$O(CO$_2$)$_6$ units and thus the charge transfer between the Zn^{2+} and the aryl carboxylates. In contrast, features assigned to H$_2$ bound to primarily organic sites cover a more narrow energy range and show low barriers to rotation consistent with the weaker binding on those sites. These sites show much larger increases in INS intensity with higher H$_2$ loading as their capacity for adsorption at the low temperature of these experiments is significantly higher. This conclusion underlines the need to explore new topologies composed of novel secondary building units from metal cations that have received less attention to increase the binding energies for H$_2$ on all sites. In particular, the use of more polarizing centers or the installment of open metal sites should enhance H$_2$ physisorption by this class of materials.
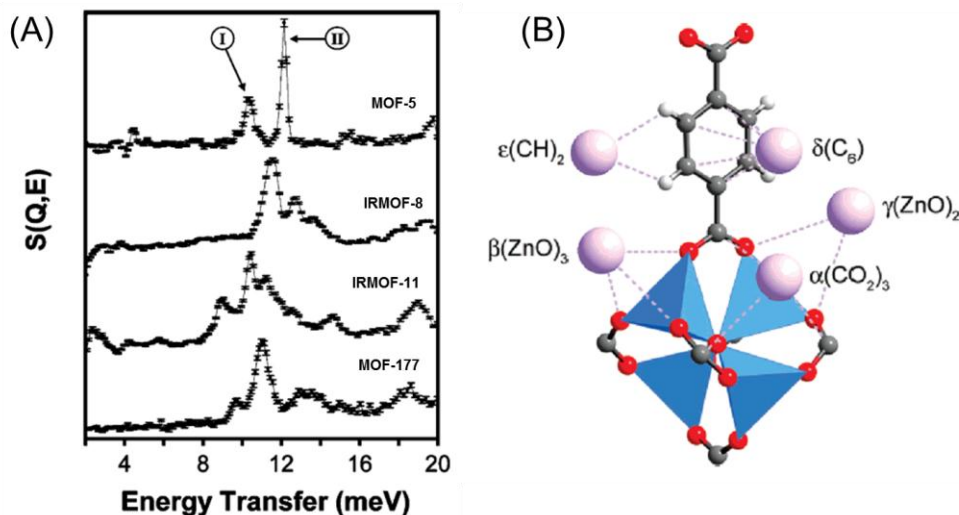

Figure 3. (A) INS spectra for MOF-5, IRMOF-8, 11 and MOF-177 loaded with 4 H$_2$ per formula unit. The two 0-1 transitions originally assigned to sites I and II in MOF-5 are labeled. Spectra are vertically offset for comparison purposes; the error bars shown are representative of all spectra. (B) Proposed binding sites for H$_2$ in MOF-5 and related frameworks in accordance with the electron density attributable to adsorbed argon (purple spheres) detected by X-ray diffraction analysis at 30 K [7]. Atom colors: C black, H white, O red, Zn blue tetrahedra.

Independent verification of high-pressure H₂ adsorption in MOF-177.

For evaluation of high pressure H₂ uptake capacity with high accuracy, although well-characterized standard materials should be useful, only limited materials show high H₂ uptake capacity even at 77 K and high pressure region. It is obvious that benchmark materials are important because the field of hydrogen storage has often suffered from reports of high H₂ uptake which were later found to be erroneous. As our DOE program officers have advised that independent measurements of H₂ uptake should be performed at a DOE-approved facility (Southwest Research Institute), H₂ uptake in MOF-177 has been measured independently.

High-pressure H₂ uptake properties for MOF-177 were evaluated by use of volumetric and gravimetric techniques. Isotherms acquired volumetrically are illustrated in Figure 4. These isotherms saturate at near 60 bar with maximum surface excess amounts of 7.0 wt%. The profiles are similar to the data which were recorded at the University of Michigan. Gravimetric measurement provides a similar profile as the volumetric isotherm measured at 77 K. The reversible isotherm indicates that H₂ is physisorbed even in the high pressure region. After buoyancy correction the uptake (surface excess amount) is 6.8 wt% at a saturation pressure of approximately 50 bar.
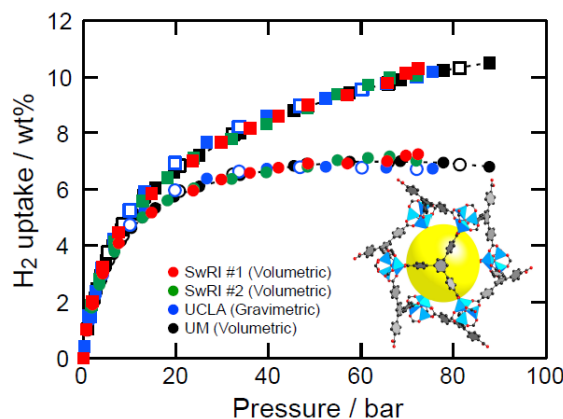
Figure 4. High-pressure H_2 isotherms for MOF-177 taken by volumetric (red, green and black circles) and gravimetric methods (blue circles). Filled and open symbols represent adsorption and desorption branches, respectively. Square symbols which are absolute adsorbed amounts are obtained (see text). Inset: crystal structure of MOF-177.

Total adsorbed amounts of H₂ are calculated using the pore volume (V_p) of MOF-177 and H₂ density at the given pressure (ρ_{bulk}); (total H₂ uptake) = (surface excess mass) + $\rho_{bulk}V_p$. Estimated absolute adsorbed amount is 10.2 wt%, which corresponds to 48.3 g L⁻¹. Since the total uptake cannot be measured experimentally, it is not possible to confirm whether or not this value is reasonable. Therefore, the total H₂ uptake was compared with N₂ adsorption data which were measured at 77 K. In contrast to the difference in gravimetric uptake, the volumes of adsorbed gases between N₂ and H₂ are close to each other (1200 and 1270 cm³ g⁻¹, respectively). Consequently, the number of adsorbed N₂ and H₂ molecules (61 and 65 adsorbates, respectively) in the formula unit is almost the same. This clearly demonstrates that the micropores in MOF-177 are in large part occupied by H₂ molecules in the high-pressure region.

Kinetic profile.

The time course profiles of adsorption and successive desorption process in MOF-177 were also recorded to illustrate their reversible and fast hydrogen uptake (and release). Figure 5 shows weight change induced by pressure change (2 - 60 bar). The time course profile clearly shows that

adsorption and desorption processes are completed within 2-5 min even though a large pressure change was applied to the experimental system. This finding is in accordance with our consideration that hydrogen molecules are physisorbed in (IR)MOFs. A similar trend was also observed in IRMOF-62, which indicates that the interpenetration does not disturb fast gas diffusion in micropores.
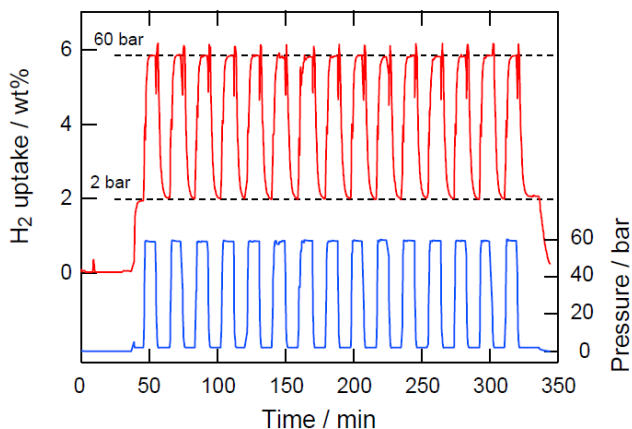

Figure 5. Kinetic profile of H_2 uptake in MOF-177 (red) by applying the pressure ranging from 2 to 60 bar (blue) was recorded at 77 K.

Exceptional H_2 saturation uptake in microporous MOFs.

Metal-oxide secondary building units (SBUs) and the organic carboxylate links of the MOFs were investigated here. The isoreticular MOF (IRMOF) series, MOF-5 (IRMOF-1), IRMOF-6, 11, 20, and 62 is derived from linking the basic zinc acetate unit, $Zn_4O(CO_2)_6$, with linear ditopic carboxylates [4]. MOF-177 is constructed from this same SBU and the tritopic link benzenetribenzoate. MOF-74 is constructed from infinite 3_1 (or 3_2) helical rods of composition $Zn_3[(O)_3(CO_2)_3]$ and MOF-14 and 199 are composed of the $Cu_2(CO_2)_4$ paddle-wheel SBU linked by tritopic linkers [8-10]. The MOFs chosen represent a subset of well characterized materials that exhibit some of the highest surface areas experimentally determined to date (Figure 1). These materials vary in chemical functionality, metrics of the link, and the nature of the SBU. Their structures are derived from non-interpenetrated nets, with the exception of the interpenetrated IRMOF-11 and 62, and three distinct SBUs. Crystalline samples of all the MOFs were prepared and activated prior to sorption measurements according to recently optimized procedures.

Figure 6A shows the resulting H_2 adsorption isotherms up to 90 bar at 77 K where saturation binding of H_2 is achieved. The isotherms do not show significant hysteresis, consistent with physisorption of supercritical H_2. The saturation uptakes vary widely: for MOF-74 the uptake at saturation (26 bar) is 2.2 wt% and 3.2 wt% for IRMOF-11 (34 bar), whereas for MOF-177 and IRMOF-20 saturation is reached between approximately 70 and 80 bar, giving H_2 uptakes of 7.0 wt% and 6.3 wt%, respectively. A plot of excess and total uptake in the gravimetric unit (wt%) as a function of BET surface area reveals a nearly linear correspondence (Figure 6A). This result stands in stark contrast to those obtained at low pressures where MOF-14, 74, 199 and IRMOF-11, the four lowest surface area materials, showed maximal uptake. This difference may arise from binding to relatively higher affinity open metal sites (present in MOF-74 and MOF-199) or to constricted pores in IRMOF-11.
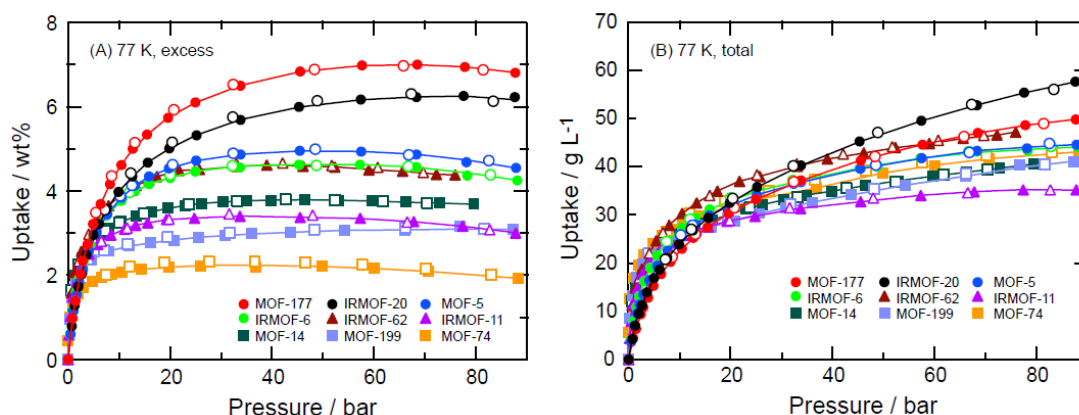
Figure 6. (A) High-pressure excess H$_2$ isotherms of MOFs at 77 K. (B) Total H$_2$ isotherms of the same MOFs in the volumetric unit.

Although gravimetric capacity is often a major target for research in H$_2$ storage materials, there are practical limits associated with the tank volume required to house the sorbent, which makes volumetric capacity just as critical a parameter to consider. Accordingly, the gravimetric total uptakes have been converted to volumetric units (g H$_2$ L^{-1}) using the crystallographic densities of each MOF (Figure 6B). By this metric, the MOF materials are much more similar in their sorption capacities due to canceling effects derived from the different densities of the materials. It should be noted that bulk packing densities will vary somewhat between materials and decrease the practical volumetric capacity in a storage system. IRMOF-20 and MOF-177 show the best uptake on a volumetric basis due to a combination of substantial H$_2$ uptake and moderate densities. The values of 57 g L^{-1} for IRMOF-20 and 50 g L^{-1} for MOF-177 are approaching the realm of the 2015 DOE system target of 40 g L^{-1}.

Ring-opening and metalation reactions within MOFs.

The strategy how to design high surface area MOFs such as MOF-177 has been developed; however, in many cases these materials do not show steep H$_2$ uptakes in the low pressure region, which is indicative of the relatively weak interaction with H$_2$. In other words, greater adsorption enthalpy is the key issue for the improvement of H$_2$ uptake at room temperature. It is likely that MOFs with accessible reactive metal sites are one of the best candidates to achieve high volumetric H$_2$ uptake capacity; therefore, the isoreticular modification of MOFs followed by the isoreticular metalation was implemented.

For the ring-opening reactions, IRMOF-3 was immersed in 1,3-propanesultone or 2-methylaziridne containing chloroform (Figure 7). The reaction products, here termed IRMOF-3b and IRMOF-3c respectively, maintained their structural topology throughout the reaction as evidenced by powder X-ray diffraction (PXRD) experiments. From elemental analysis (EA), the approximate reaction yield per organic linker of IRMOF-3b and IRMOF-3c was estimated to be 57% and 108%, respectively.
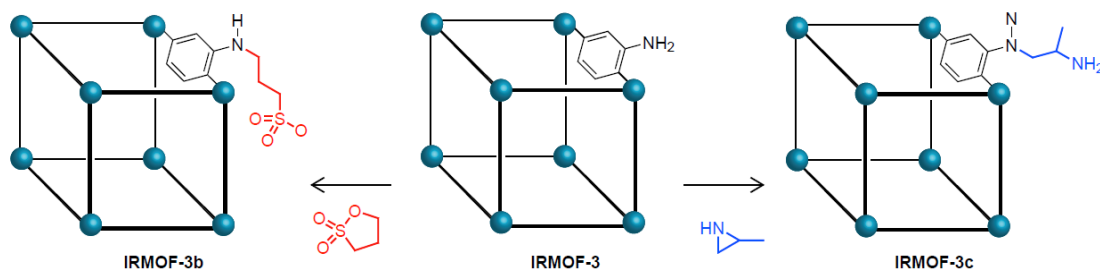
Figure 7. Ring-opening reactions performed on IRMOF-3 leading to covalently functionalized products IRMOF-3b and 3c. The cage of the MOF is represented as a cube where blue balls replace Zn_4O units and edges replace the organic linkers.

The high porosity of the parent IRMOF-3 structure is retained after reaction, as evidenced by N_2 adsorption isotherms collected for the reaction products. IRMOF-3b has the BET surface area of 1380 m^2 g^{-1}, which is 67% of IRMOF-3. This reduction in surface area is expected with the added mass of the alkylsulfonate groups. IRMOF-3c has a BET surface area of 530 m^2 g^{-1}, 26% of IRMOF-3. This reduction is more than what is expected for the added mass of alkylamine groups, though the material is still highly porous.

Originally IRMOF-3c was immersed in the solution containing Fe(II) ions for the metalation reaction. However, the metal composition of the IRMOF-3 derivative implies that zinc ions leached out from the IRMOF and were coordinated to alkylamine groups. Therefore, a new amino-functionalized MOF with a larger cavity (termed MOF-202) was prepared. The topology (connectivity) of MOF-202 is the same as MIL-101 [11]. Since MOF-202 has large pore openings (> 10 Å) and two types of large cages (25 – 30 Å), it was expected that the pore aperture/diameter of MOF-202 after the reaction with aziridine would remain large enough for gas diffusion. However, the BET surface area of MOF-202n (modified material) was much smaller than that of the pristine material (2000 and 525 m^2 g^{-1} for MOF-202 and MOF-202n, respectively). The reason for the surface area decrease is not clear, but pore openings of MOF-202n could be partly blocked by the post-modification process.

After modification, MOF-202n was immersed in a solution containing Cr(III) ions (terms MOF-202n-Cr). The BET surface area of MOF-202n-Cr was estimated to be 200 m^2 g^{-1}, which is smaller than MOF-202n probably due to the mass added as a result of metal impregnation. H_2 isotherms for MOF-202n and MOF-202n-Cr at 77 K were also measured. The metal impregnated material shows slightly better H_2 uptake behavior in the very low pressure range; however, the adsorbed H_2 amount in these MOFs (0.46 and 0.41 wt% for MOF-202n and MOF-202n-Cr) are much smaller than in the pristine sample (1.57 wt% for MOF-202). This deficit indicates that higher surface area is a prerequisite for the reasonable H_2 uptake. Based on the 77 and 87 K isotherms, the Q_{st} of H_2 was estimated. Unexpectedly, the impregnated compound shows smaller Q_{st} value (7.1 kJ mol^{-1}) compared to MOF-202n (9.9 kJ mol^{-1}), indicating that there is no strong Cr-H_2 interaction in this system. The sample was heated to 200 °C for two days to remove any solvent occluded in the pores; however, even after heating the profile of the H_2 isotherm for MOF-202n-Cr did not change.

Isoreticular metalation of MOFs.

Although metal impregnation experiments were performed using two new MOFs, it is still not clear how the metals were bound to the organic functionalities. The lack of the information on the metal coordination sites may hamper the understanding of any metal-H_2 interaction. Another MOF system $((Zn_4O)_3(NH_2\text{-}BDC)_3(BTB)_4)$ [12,13] was chosen to implement the isoreticular covalent modification and successive metalation (Pd coordination). After reaction with a palladium salt, almost 100% of metal coordination sites were occupied by palladium ions. In general it is not easy to determine the metal coordination environment within the framework based on elemental analysis and conventional X-ray diffraction techniques. Therefore, the metal coordination environment was investigated by Pd K-edge extended X-ray absorption fine structure spectroscopy (EXAFS).

Crystals of $(Zn_4O)_3(NH_2\text{-}BDC)_3(BTB)_4$ (Figure 8, **A**), were reacted with 2-pyridinecarboxaldehyde to form the covalently bound iminopyridine chelate derivative, $(Zn_4O)_3(C_6H_5N_2\text{-}BDC)_3(BTB)_4$ (**B**), which was reacted with $PdCl_2(CH_3CN)_2$ to give the metal-complexed MOF, $(Zn_4O)_3(C_6H_5N_2PdCl_2\text{-}BDC)_3(BTB)_4$ (**C**). Remarkably, these reactions and their respective products are achieved without loss of structural order or framework connectivity.

The porosities of **B** and **C** were confirmed by Ar adsorption measurements at 87 K (the BET surface areas for **B** and **C** are 3200 and 1700 $m^2 \ g^{-1}$, respectively). It is worth noting that both materials maintain porosity after two subsequent chemical transformations. Additionally, Type IV isotherms are observed in all samples (**A**-**C**). It is also noted that compounds **B** and **C** were activated on a supercritical CO_2 dryer [14], and no sample degradation under the supercritical conditions was observed.
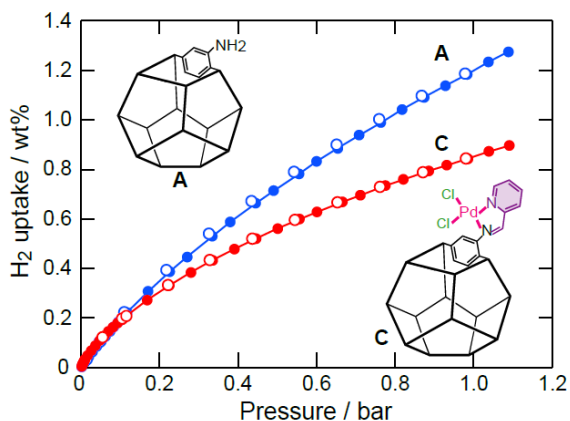
Figure 8. Low-pressure H_2 isotherms for compound **A** (blue) and **C** (red) measured at 77 K. Molecular structures of **A** and **C** (before and after functionalization, respectively) are shown as cage structures.

Figure 8 demonstrates low-pressure H_2 isotherms for compounds **A** and **C**. H_2 uptake in **C** is 0.9 wt% at 77 K and 1 bar, which is smaller than that in **A** due to the smaller BET surface area. However, the heat of adsorption profile for **C** is improved by metalation (the Q_{st} values at zero-coverage for **A** and **C** are 5.7 and 6.6 kJ mol^{-1}, respectively). The successful isoreticular covalent transformation followed by metalation opens a route for incorporating metal ions into a wide range of frameworks. This is an important first step toward exploiting such metalated frameworks in gas-storage applications.

Synthesis of MOFs with bipyridine links.

A new Al-MOF (MOF-253) [15] with 2,2′-bipyridine-5,5′-dicarboxylate (BPyDC) link by solvothermal synthesis was prepared. The reasons why this system was chosen are as follows; (i) two nitrogen atoms in the organic link can hold metals, while these metals do not form small molecules (e.g. $M(BPy)_3$), (ii) higher stability compared to Zn-MOFs, (iii) simple and scalable synthetic procedure, (iv) prevention of metal exchange during the metal impregnation process, and (v) relatively long ditopic link is advantageous for providing reasonable surface area and pore volume even after the metal impregnation.

The structure of MOF-253 ([Al(OH)(BPyDC)]) was confirmed by powder X-ray diffraction measurements and elemental analysis. The BET surface area is calculated to be 1380 m^2 g^{-1}, and its H_2 uptake at 77 K and 1 bar is 1.4 wt%. To implement metal impregnation, originally pristine MOF-253 was immersed in the solution containing Sc(III), Cr(III), Fe(II), Fe(III), and Mn(II) ions. However, the loaded amounts of metal were not very high. Therefore, MOF-253 was reacted with $PdCl_2(CH_3CN)_2$ or $PtCl_2(PhCN)_2$ (MOF-253-Pd and MOF-253-Pt, respectively). Here, the amount of metal used was calculated based on the Al/Pd ratio; MOF-253-Pd (100%) indicates Al/Pd (or Pt) ratio = 1. Obtained metalated MOFs were analyzed to confirm that the Pd/Pt is complexed to the BPyDC unit and to precisely determine the Pd/Pt coordination environment within the framework by extended X-ray absorption fine structure (EXAFS) spectroscopy. Based on the best fitting data of Pd/Pt K-edge EXAFS Fourier transforms, it was confirmed that these metal ions were successfully bound to the bipyridine moieties in MOFs. Additionally, analysis of the X-ray absorption near-edge structure (XANES) spectrum indicated that the major chemical forms of Pd/Pt within MOF-253 were consistent with bidentated metals to bipyridine and not the starting materials.

Figure 9A demonstrates N_2 isotherms of Pd metalated MOF-253. After the metal impregnation, the BET surface area of the MOF was drastically dropped compared to pristine MOF-253 (BET surface area: 90 m^2 g^{-1} for MOF-253-Pd(100%), 1380 m^2 g^{-1} for pristine MOF-253). This is much lower than expected surface area (580 m^2 g^{-1} based on *Cerius2*) where the composition of metalated material would be [Al(OH)(BPyDC)PdCl_2]. TGA analyses were performed to see if any occluded solvent is observed; however, there is no significant weight loss due to free solvent molecules. To mitigate the surface area drop, metal concentration was modified. However, observed surface area did not change when 50% concentration of metal was loaded (only Pt data was shown in Figure 9A). In contrast, when the Al/Pd ratio is 5/1, the BET surface area (640 m^2 g^{-1}) was greater than MOF-253-Pd(100%) and MOF-253-Pd(50%).

Currently, the reason for the significant surface area decrement is not clear. One of the possible explanations is that the shape of 1-D channel was distorted due to the presence of guest molecules. This has been demonstrated before through research on MIL-53 analogues, which showed the pore volume could be lowered when guest molecules were present [15]. The low-pressure H_2 isotherms for MOF-253 derivatives are illustrated in Figure 9B. The H_2 uptakes are influenced by impregnated metal amounts and higher loading materials show small hysteresis. Because of the significant surface area decrement, the H_2 uptakes are not exceptional. However, since the H_2 uptake per surface area is still high, it is believed that higher H_2 uptakes could be achieved if the sample activation procedure is optimized.
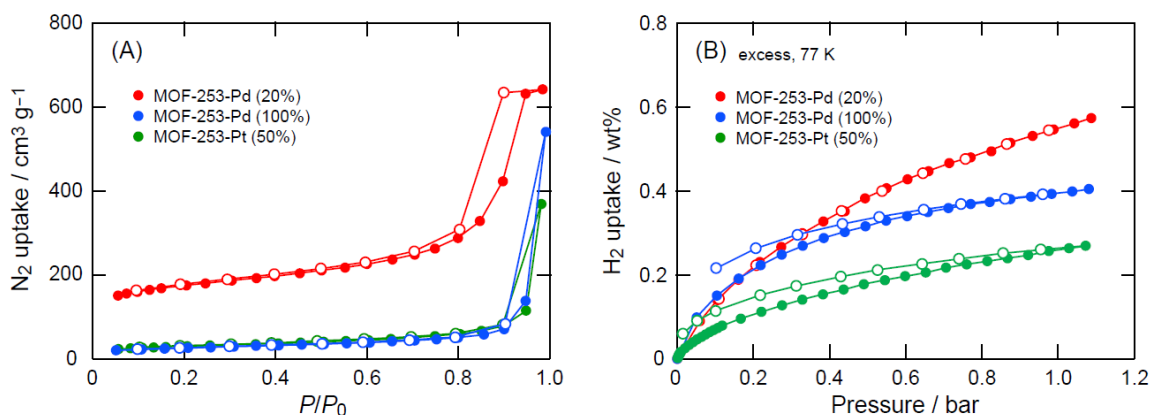
Figure 9. N_2 (A) and H_2 isotherms (B) for metalated MOF-253 measured at 77 K.

Ultrahigh porosity in MOF-200 and 210.

Two of the most important properties of MOFs are their high porosities and high specific surface areas. An important consideration in maximizing the uptake of H_2 within MOFs is to increase the number of adsorptive sites within a given material. The simplest way to accomplish this is to use slim organic linkers in which the faces and edges of the constituent units are exposed for gas adsorption [2]. As shown in MOF-5 and MOF-177, the octahedral $Zn_4O(CO_2)_6$ has had a prominent role as a building unit in producing structures exhibiting exceptional porosity [1,2]. Therefore, the expanded forms of MOF-177 from BBC were prepared to give MOF-200, and used mixed BTE/BPDC links to obtain MOF-210 (Figure 10).
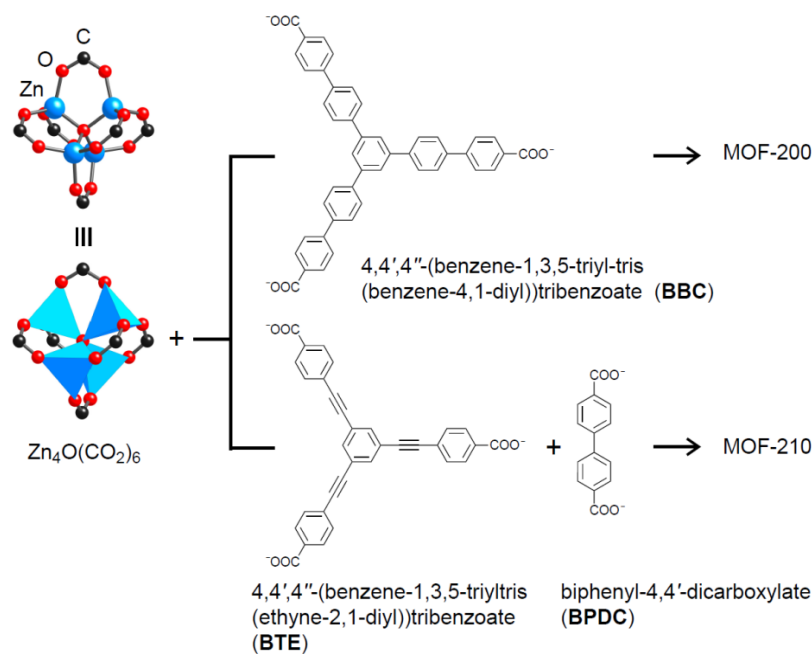
Figure 10. $Zn_4O(CO_2)_6$ unit (left) is connected with organic linkers (middle) to form MOFs.

MOF-200 and 210 were prepared from a solvothermal reaction of organic linkers and zinc nitrate, and the resulting crystals were characterized by single crystal X-ray diffraction. Considering the bulk density and void space calculated from the crystal structure analyses, MOF-200 and 210 are promising candidates to realize ultra-high surface area. However, preliminary trials revealed that the solvent exchange followed by pore evacuation under vacuum was not effective to activate MOF-200 and 210 without losing porosity. Therefore, these crystals were fully exchanged with liquid CO_2, kept under supercritical CO_2 atmosphere, followed by their pores being bled of CO_2 to yield activated samples. Successful guest removal was confirmed by PXRD measurements and elemental analyses.

As shown in Figure 11A, these MOF samples show distinctive steps ($P/P_0 = 0.14$ and 0.27 for MOF-200 and 210), and the profiles for MOF-200 and 210 are nearly the same as the predicted isotherms by grand canonical Monte Carlo (GCMC) simulations (Prof. Snurr group (Northwestern Univ.)). The maximum N_2 uptake capacities at 77 K in MOF-200 and 210 are 2340 and 2330 cm^3 g^{-1}, respectively. More importantly, the measured values are near the values predicted based on the structure, indicating that these materials are well-activated. Because of the successful sample activation, extremely high BET (and Langmuir) surface areas were obtained: 4530 (10400) and 6240 (10400) m^2 g^{-1} for MOF-200 and 210. The BET surface area of MOF-210 is the highest reported for crystalline materials.
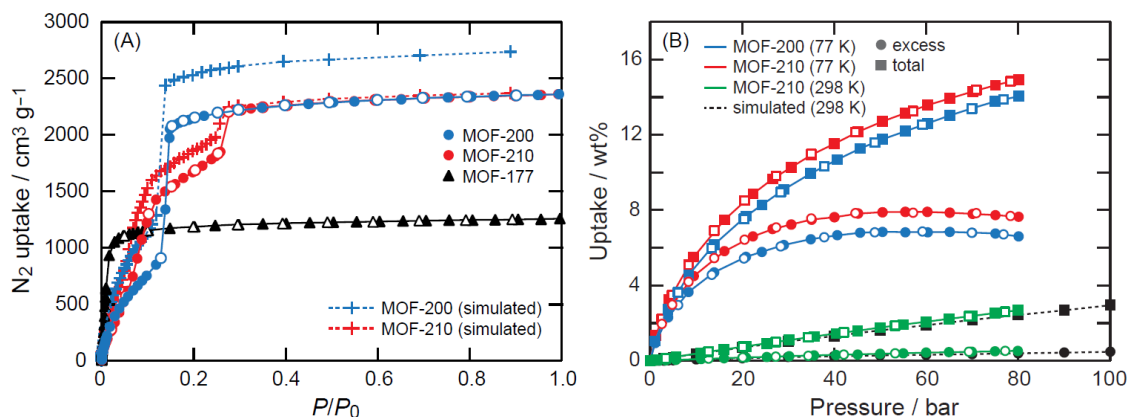
Figure 11. (A) Low-pressure N_2 isotherms of MOF-177, 200, and 210 at 77 K. Simulated isotherms of MOF-200 and -210 were overlaid. (B) High-pressure H_2 isotherm of MOF-200 (blue circles) and 210 (red circles) measured at 77 K. Experimental (green) and simulated (black) H_2 isotherm of MOF-210 at room temperature are overlaid. Squares in the same color symbols represent calculated total uptake of H_2 under the same conditions.

Given the exceptional properties of such materials, it is expected that these high surface area MOFs would exhibit exceptional H_2 storage capacity. These MOFs reach saturation uptakes, and the saturation pressure increases with an increase in the cavity size (Figure 11B). The surface excess H_2 uptake in MOF-210 (7.9 wt%) was higher than MOF-177 and 200 (6.8 and 6.9 wt%) [16]. Given the pore volume and density of H_2 at 77 K, the total H_2 uptake in MOF-210 is

calculated to be 15 wt%, which exceeds that of typical alternative fuels (methanol and ethanol) and hydrocarbons (pentane and hexane). MOF-200 also shows large total uptake (14 wt%); again, these values are higher than MOF-177 [16]. However, the volumetric total uptake (44 g L^{-1} for MOF-210; 36 g L^{-1} for MOF-200) was smaller than MOF-177 (50 g L^{-1}). The trend indicates that it is better to reduce the dead volume by introducing functionalities, which can interact positively with H$_2$.

Figure 11B displays the H$_2$ isotherms of MOF-210 at 298 K. The excess uptake at 80 bar was 0.53 wt%, which is similar to the H$_2$ uptake by MOF-177 (0.54 wt% at 80 bar and 298 K). It is believed that the excess H$_2$ uptake was not improved because of the average pore diameter of MOF-210. The average pore diameter of MOF-210 is larger than the DOE recommendation for pore diameter size (0.7-1.2 nm to maximize the room temperature H$_2$ uptake capacity) with a significant storage space that still remains.

Calculated total H$_2$ isotherm is also shown in Figure 11B. The total uptake at 80 bar was 2.7 wt%, which is the highest number reported for physisorptive materials. When the bulk density of MOF is applied, the volumetric H$_2$ uptake is calculated to be 6.9 g L^{-1} at 80 bar. Although the majority of the total uptake is attributed to the large pore volume (i.e. the contribution from $\rho_{bulk}V_p$), the volumetric H$_2$ uptake by MOF-210 remains higher than the bulk density of H$_2$ under the same conditions. Worth noting is that this finding is in sharp contrast to the fact that MOFs with larger density typically show even smaller volumetric uptakes than the bulk H$_2$ density.

Through the collaborative work with Prof. Goddard group (Caltech), room temperature H$_2$ uptake by MOF-210 was predicted. As shown in Figure 11B, these room temperature high-pressure H$_2$ data are in good agreement with predicted excess and total isotherms. However, H$_2$ isotherms recorded at room temperature sometimes contain significant errors due to their smaller uptake (compared to 77 K data). Therefore, it is fair to say that the simulation data provides reassuring support for the excellent experimental room temperature H$_2$ uptake capacity by MOF-210.

Scaling-up and cost of MOFs.

The synthesis of MOFs is usually performed by solvothermal methods: heating a mixture of organic linker and metal salt in a solvent system that usually contains formamide functionality. These methods often yield crystals suitable for single crystal X-ray diffraction analysis; however, there are several disadvantages as follows: (i) the reaction rate is relatively slow (1 to 7 days), (ii) solvothermal conditions are sometimes unsuitable for the large scale synthesis (> 100 mL), and (iii) the heating cost for the system is not negligible. Considering the requirements of adsorbent cost ($100 /kg), it is necessary to develop inexpensive and simple synthetic procedures. Through a long-standing collaboration with BASF, room temperature synthesis of MOFs for four well known MOFs: MOF-5, MOF-74, MOF-177, and MOF-199 [17] have been developed. Typically, for the MOF-5 synthesis, H$_2$BDC (5.065 g, 30.5 mmol) and triethylamine (8.5 mL) were dissolved in 400 mL of *N*,*N*-dimethylformamide (DMF). Zn(OAc)$_2$·2H$_2$O (16.99 g, 77.4 mmol) was dissolved in 500 mL of DMF. The zinc salt solution was added to the organic solution with stirring over 15 min, forming a precipitate, and the mixture was stirred for 2.5 h. This reaction also proceeds without triethylamine. These findings would be helpful to provide porous MOFs with inexpensive cost. Indeed, our simple calculation provides a ballpark where the reagent cost (i.e. price of H$_2$BDC and Zn(OAc)$_2$·2H$_2$O from Aldrich) cost for 1 kg of MOF-5 is only $2.

Therefore, it is believed that highly porous MOFs with simple organic linkers would be available at a reasonable price.

Next steps for room temperature H$_2$ storage.

   The results in this project show that open metal sites can provide large binding energy sites for H$_2$. However, when such open metal sites are occupied by H$_2$, observed Q_{st} value drops to 5 kJ mol^{-1}. This phenomenon is the primary reason for why the majority of excess H$_2$ uptake in such materials is observed below 5 bar. It should be noted that, if the Q_{st} value is constant up to high-pressure range, the profile of the isotherm must be linear in this range. In other words, excess H$_2$ uptake is proportional to the pressure. This implies that higher density of strong binding sites is important rather than a significantly large Q_{st} value. Furthermore, it is known that heterogeneity (due to the coexistence of strong and weak binding sites) typically reduces delivery amount of H$_2$ [18]. Is there any good strategy to increase the number of binding sites? If 40 g L^{-1} of H$_2$ is stored through one-to-one binding in MOF-5, the necessary required H$_2$ binding sites can be estimated to be 207 per unit cell (which corresponds to 6.3 wt% H$_2$ uptake). Considering that there are only 328 non-hydrogen atoms (C, O, and Zn) per MOF-5 unit cell, it is unlikely that MOF-5 can meet the volumetric target. This indicates that the realistic strategy is to introduce strong H$_2$ binding sites in the porous solids, where each binding site can capture multiple H$_2$ molecules. For example, if each phenyl group in MOF-5 holds two metal Li atoms and if each Li atom can bind 4.3 H$_2$ molecules, the expected H$_2$ uptake approaches 40 g L^{-1} (= 6.0 wt%). A similar idea has been reported through theoretical calculations [19]. On the contrary, it is not straightforward to introduce such metals because these metal moieties will easily be capped by organic solvent and water molecules. However, as a general approach, metalation of MOFs with high-valence metals is promising and provides a rational direction to realize high volumetric H$_2$ density near room temperature.

Concluding Remarks

   The aim of this project is to develop the next generation of MOFs. Based on the systematic study, the fundamentals of H$_2$ storage in MOFs were gleaned. For instance, the importance of the open metal sites was proposed for the first time, and this is also the origin of the new strategy termed isoreticular functionalization and metalation. It is believed that the H$_2$ adsorption behavior of MOFs would be improved by the addition of strong binding sites; however, a large pore volume is still a prerequisite feature. From the viewpoint of the storage space (i.e. H$_2$ density in canisters), synthesis of ultrahigh surface area MOFs were implemented. After many trials the optimal synthetic condition and effective activation method were developed, leading to 15 wt% of total H$_2$ uptake at 80 bar and 77 K. More importantly, the total H$_2$ uptake by MOF-210 was 2.7 wt% at 80 bar and 298 K, which is the highest number reported for physisorptive materials. In the project period, experimental H$_2$ uptake at room temperature did not meet the DOE system targets; however, it is believed that the concept of the isoreticular metalation of extremely porous MOFs is one of the best strategies to pursue practical storage targets.

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