

Significantly Enhanced Hydrogen Storage in Metal–Organic Frameworks via Spillover

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The commercialization of fuel-cell powered vehicles is limited by the lack of a safe and effective method for hydrogen storage.¹ None of the currently available candidate storage systems is capable of meeting the DOE criteria for use in transportation.^{2,3} Concerning adsorbents, nanostructured carbons including carbon nanotubes, graphite nanofibers, and activated carbon have been the major candidates for hydrogen storage due to their light weight and high surface areas. However, recent reports show that, at ambient temperature, known carbon nanostructures cannot store a sufficient amount of H₂ required for transportation applications.^{1–3}

Recently, a new class of porous metal–organic frameworks (MOFs) has attracted much attention because of their potential applications in adsorption and separation processes.⁴ In particular, cubic frameworks consisting of tetrahedral [Zn₄O]⁶⁺ clusters linked by organic units were discovered to adsorb H₂ reversibly up to 1.6 wt % at 77 K and 1 atm.⁵ Inelastic neutron scattering studies of molecular H₂ adsorbed in MOFs indicated that both the metal-oxide clusters and the organic units are the adsorption sites for hydrogen.^{4a} Therefore, the hydrogen storage capacities of MOFs can be significantly modified by replacement of Zn²⁺ with other similar metal ions, such as, Mg²⁺, Ni²⁺, or Cu²⁺, or/and a variation of the organic linking units.^{4–8} Férey et al. reported a high hydrogen storage capacity of 3.8 wt % in the metal–benzodicarboxylate Al(OH)(O₂C–C₆H₄–CO₂), MIL-53, at 77 K and 1.6 MPa.^{4d} However, no significant hydrogen uptakes on the MOFs have been obtained at room temperature.

We have suggested the use of dissociation/spillover for H₂ storage^{9a} and have demonstrated that it is possible to use secondary spillover to increase the storage capacities in nanostructured carbon materials by using a catalyst that is capable of dissociating H₂.⁹ In this communication we report, for the first time, significantly enhanced hydrogen adsorption in MOFs via spillover at room temperature over a wide range of pressure. By using a very simple technique to cause spillover, the storage capacity of IRMOF-8 was increased to 1.8 wt % at 298 K and 10 MPa. This represented an enhancement factor of 3.1. Furthermore, the storage was totally reversible.

MOF-5 (also known as IRMOF-1) and IRMOF-8 were synthesized by a direct mixing method developed by Huang et al. (see Supporting Information for details on synthesis and characterization).^{10,11} For spillover experiments, a catalyst containing 5 wt % Pt supported on active carbon was used for dissociation of H₂. Here, active carbon was the primary receptor for hydrogen spillover.^{9c,12} The catalyst and the secondary spillover receptor (MOF-5 or IRMOF-8) (at a weight ratio of 1:9) were ground together (with mortar and pestle, for 1 h) to produce the physical mixture.

The H₂ storage characteristics of MOF-5, and IRMOF-8 at 77 K and at pressures <1 atm are shown in Figure 1. The H₂ adsorption on MOF-5 or IRMOF-8 at 77 K shows a reversible type-I isotherm characteristic of a microporous material. In addition, the isotherms show no hysteresis upon desorption. Thus, the isotherms are totally reversible. The hydrogen uptakes are 1.28 wt % for MOF-5 and

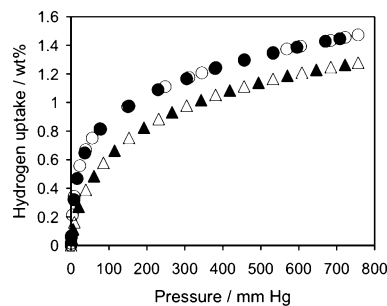


Figure 1. H₂ isotherms for MOF-5 (triangles) and IRMOF-8 (circles) at 77 K. Open symbols: adsorption branch; filled symbols: desorption branch.

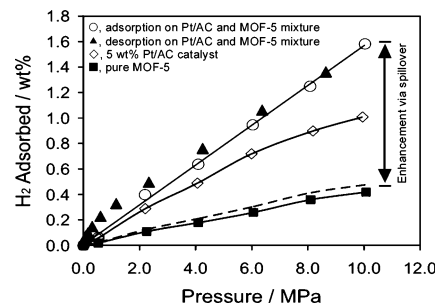


Figure 2. High-pressure hydrogen isotherms at 298 K for MOF-5. Dotted line is prediction based on the weighted average of the mixture.

1.48 wt % for IRMOF-8 at 1 atm and 77 K. The H₂ storage capacities of MOF-5 and IRMOF-8 obtained in this study are in good agreement with Panella and Hirscher¹⁰ and the latest corrected results of Roswell et al.,⁵ under the same conditions. In addition, the H₂ isotherms measured at 77 K (0–1 atm) did not show saturation. Therefore, higher H₂-adsorption capacities can be expected at elevated pressures.

High-pressure H₂-adsorption measurements were performed on a specially designed Sievert's apparatus using a static volumetric technique. The apparatus and our measurement procedure have been proven highly accurate and reproducible by calibration using LaNi₅ alloy powder that forms hydride.^{9d} To determine the enhancing effect of spillover on pure MOF-5 and IRMOF-8, the hydrogen isotherm on the Pt/AC catalyst was also measured under the same conditions. As shown in Figure 2, unmodified MOF-5 has a hydrogen storage capacity of ~0.4 wt % at 298 K and 10 MPa. For comparison, MOF-5 was reported to have a H₂ uptake of ~0.3 wt % under the same conditions.¹⁰ The slightly higher hydrogen adsorption amount obtained in this study is in agreement with a higher BET surface area (1021 m² g⁻¹) and a higher micropore volume (0.39 cm³ g⁻¹) than that by Panella and Hirscher (572 m² g⁻¹ and 0.28 cm³ g⁻¹, respectively).¹⁰ Moreover, our surface area and pore volume values are in agreement with that reported by Huang et al.¹¹ The hydrogen uptake of Pt/AC at 10 MPa was about 1.0 wt %. It is clear that hydrogen spillover has occurred on the surface of active carbon, as reported in previous literature.^{12,13} The expected H₂ capacity of the mixture of Pt/AC and MOF-5 is shown by the

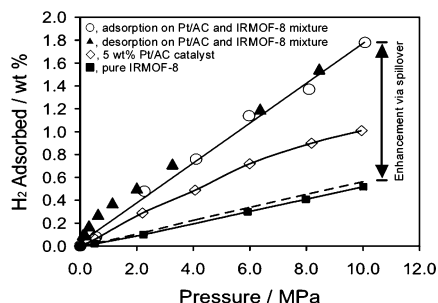


Figure 3. High-pressure hydrogen adsorption isotherms at 298 K for IRMOF-8. Dotted line is prediction based on the weighted average of the mixture.

dotted line in Figure 2, by taking weighted average (assuming additivity). However, as shown in Figure 2, the H_2 uptake was substantially higher than the expected values at all pressures. This significant enhancement was clear evidence of secondary spillover of H atoms to MOF-5, as a secondary receptor. The enhancement factor (see Supporting Information for definition) was ~ 3.3 , i.e. the hydrogen uptake of MOF-5 at 10 MPa was increased by a factor of 3.3. There is no apparent saturation value for the physical mixture, even at 10 MPa. Reversibility was assessed by measuring the desorption branch down to 1 atm. It can be seen from Figure 2 that the desorption branch almost followed the adsorption branch, although there appeared to be a slight hysteresis. The sample was then evacuated to a pressure of 1 Pa (7.5×10^{-3} Torr) for 12 h at 298 K. The second adsorption branch was in complete agreement with the first adsorption branch. This result indicates full reversibility.

Similarly remarkable enhancement of H_2 storage capacity by spillover was also observed on IRMOF-8, shown in Figure 3. The H_2 uptake on pure IRMOF-8 prepared in this study was ~ 0.5 wt % at 298 K and 10 MPa. By applying the simple spillover technique, on a Pt/AC and IRMOF-8 physical mixture (at 1:9 weight ratio), the hydrogen adsorption amount was increased to 1.8 wt % under the same conditions (i.e. by an enhancement factor of 3.1). The amount was much lower if the IRMOF-8 sample was prepared with the procedure of Yaghi and coworkers.⁵ This uptake is equivalent to 8.3 H_2 (or 16.6 H atoms) per formula unit, which is well below the saturation limit of IRMOF-8.^{4a} Furthermore, the adsorption was also totally reversible and did not show any saturation up to 10 MPa, similar to results on the MOF-5 receptor.

The H_2 uptakes for both pure IRMOF-8 and IRMOF-8 modified with catalyst were higher than that for the corresponding MOF-5 samples. Attempts to correlate the specific surface area and hydrogen uptake have been made for nanostructured carbon materials in several reports.¹⁴ However, a similar correlation has not been established for MOF materials.^{5,15} Our results agree with the earlier observation that large surface area and pore volume are not the only factors for high H_2 storage,^{4f} because in the present work both surface area and pore volume of IRMOF-8 were lower than those of MOF-5 (see Supporting Information, Table S1). The difference in H_2 capacity between MOF-5 and IRMOF-8 can be attributed to differences in the organic units that have been considered as important adsorption sites.^{4a} Therefore, MOFs with more rings in the organic linker could be expected to have even higher H_2 storage capacities. On the other hand, the results shown in Figures 2 and 3 would suggest that the H_2 capacity of the pure MOF is a major factor in determining the overall H_2 uptake via spillover.

It has been proposed by Robell et al. that H_2 molecules are adsorbed rapidly on Pt sites and then diffuse slowly away from them to active carbon.¹² It was observed that a complete saturation of isotherm took more than 1 h on the Pt/AC samples. In this investigation, over 40% of the total H_2 adsorption capacity at each pres-

sure was reached in about 10 min. In 1 h, nearly 70% of H_2 was adsorbed. A complete uptake of H_2 would roughly take over 3 h, especially at higher pressures. For desorption, it was observed that over 60% of the adsorbed hydrogen was released in 10 min when the pressure was decreased to a lower pressure.

In conclusion, we have demonstrated that hydrogen storage by spillover is a promising technique to achieve significant hydrogen storage by MOFs. The spillover enhancement factors for MOF-5 and IRMOF-8 were 3.3 and 3.1, respectively. The highest measured reversible H_2 uptake was 1.8 wt % at 298 K and 10 MPa on a Pt/AC and IRMOF-8 physical mixture. These results are attractive because it can be speculated that the spillover and hence the enhancement of capacities can also be observed on other metal-organic frameworks (MOFs) or similar porous materials because of their similar structures as MOF-5 and IRMOF-8. Additionally, as reported in our previous investigation, the hydrogen uptake of a physical mixture of primary spillover source and a secondary receptor can be further enhanced by building a carbon "bridge" between the two components to improve the contacts between them.^{9d} Therefore, we anticipate that further increases in performance can be expected, with new MOFs having similar but larger organic linkers, and exploring an effective bridging technique to enhance contacts and hence spillover over MOFs. This is under investigation, and results will be reported shortly.

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Supporting Information Available: Experimental details, N_2 adsorption results, FT-IR spectra, and powder XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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