

Alkali Metal Cation Effects on Hydrogen Uptake and Binding in Metal-Organic Frameworks

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A 2-fold interwoven metal-organic framework has been chemically reduced and doped with Li^+ , Na^+ , and K^+ . At low pressures and temperatures, the reduced and doped materials exhibit enhanced H_2 uptake—up to 65% higher than for the neutral framework. Notably, at similar doping levels, H_2 binding is strongest with Li^+ and decreases as $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. However, the uptake increases in the opposite order. We attribute the behavior to structural changes accompanying framework reduction.

The deployment of hydrogen as a carbon-free fuel source is dependent on its safe and efficient production, transport, and storage.¹ Molecular physisorption of hydrogen is a potentially attractive approach to storage, as uptake and discharge are likely to be much faster than in materials that dissociatively store hydrogen. Permanently microporous metal-organic frameworks (MOFs) are being explored as H_2 storage materials, in part because pore size and shape as well as pore-wall chemical composition are readily tuned by the choice of organic strut.² Additionally, the high surface areas, high micropore volumes, and low densities of MOFs suggest that molecular hydrogen should be storable at a high density; notably, 7.5 wt % H_2 uptake was recently demonstrated in MOF-177—albeit at 77 K.³ Extending the performance to ambient temperature will require substantial improvement in the H_2 heat of adsorption.⁴ The predicted average H_2 heat of adsorption necessary for effective ambient temperature storage and release, ca. 15 kJ/mol,^{5,6} is still well beyond the highest reported values.

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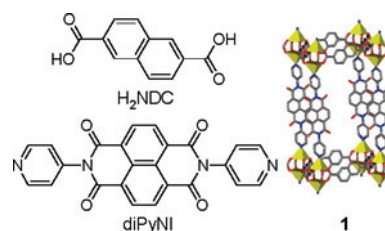


Figure 1. Chemical structure of ligands in **1** and the crystal structure of **1** omitting the interwoven second network. Hydrogens are omitted for clarity. The yellow polyhedra represent the zinc ions. Carbon: gray. Oxygen: red. Nitrogen: blue.

Much of our effort to understand and enhance H_2 uptake in MOFs has been aimed at the amplification of heats of adsorption through framework reduction and concomitant cation doping.⁷ Here, we report on the dopant-cation dependence of H_2 uptake and binding in a 2-fold interwoven MOF, $\text{Zn}_2(\text{NDC})_2(\text{diPyNI})$ (NDC = 2,6-naphthalenedicarboxylate; diPyNI = *N,N'*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide), designated **1** (Figure 1).⁸ From previous work with this material, we hypothesized that variation of the extra-framework cation could differentially affect H_2 uptake by two complementary mechanisms: the introduction of strong H_2 binding sites (sites for charge (cation)–quadrupole (H_2) interaction)⁹ and cation-induced shifts in the interwoven networks.

Previously, we have engendered framework reduction through direct contact of the MOF with solid lithium metal.⁷ Since here we are interested in changing the cation and monitoring structure and adsorption performance, we chose to use the well-understood metal-naphthalenide reductants, $\text{M}(\text{NAP})$, where $\text{M} = \text{Li}, \text{Na}, \text{or } \text{K}$.¹⁰ Conveniently, the naphthalenide anion is intensely green in solution. When added to **1**, the solution turns colorless, while **1** itself changes from yellow to deep green/brown, consistent with electron transfer from the naphthalenide

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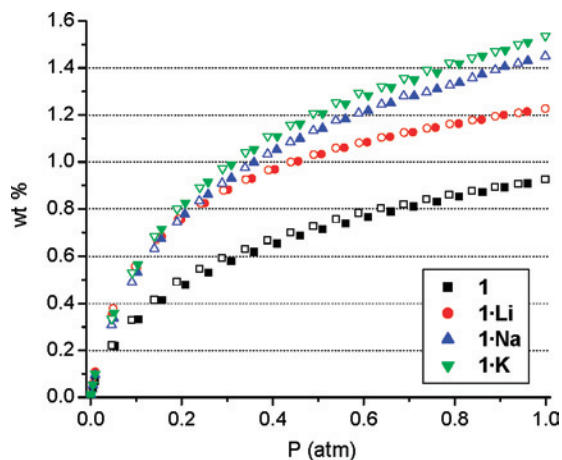
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Table 1. Summary of N₂ and H₂ Low-Pressure and Temperature Adsorption Measurements of **1** and **1•M**

| | M/ diPyNI | BET surface area (m ² /g) ^a | DR micropore volume (cm ³ /g) ^b | H ₂ wt % (1 atm, 77 K) | Q _{st} range (kJ/mol) | average Q _{st} (kJ/mol) | additional H ₂ /M ⁺ at P(H ₂) = 1 atm |
|--------------|--------------|--|--|--|--------------------------------------|--|--|
| 1 | 0.00 | 802 | 0.30 | 0.93 | 5.6–3.4 | 4.31 ± 0.61 | n.a. |
| 1•Li | 0.06 | 676 | 0.34 | 1.23 | 6.3–5.6 | 5.96 ± 0.18 | 24 |
| 1•Na | 0.10 | 837 | 0.33 | 1.45 | 5.6–4.5 | 4.99 ± 0.31 | 25 |
| 1•K | 0.06 | 988 | 0.39 | 1.54 | 6.0–3.3 | 4.51 ± 0.72 | 49 |
| 1•K' | 0.26 | 813 | 0.32 | 1.42 | 5.6–3.7 | 4.46 ± 0.47 | 9 |
| 1•K'' | 0.84 | 382 | 0.15 | 0.75 | 5.1–4.0 | 4.45 ± 0.32 | (1) |

^a BET surface area determined from the N₂ adsorption isotherm between 0.007 < P/P₀ < 0.04. ^b DR micropore volume calculated at P/P₀ < 0.01

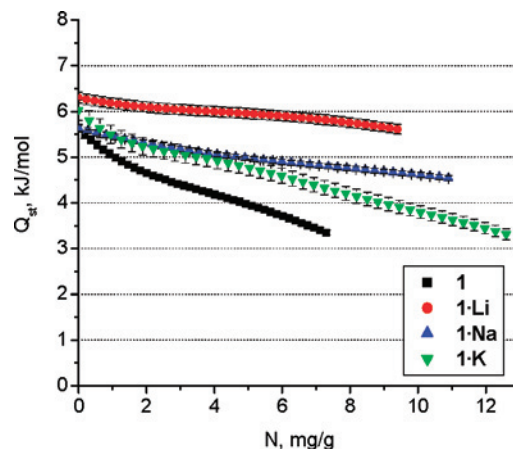
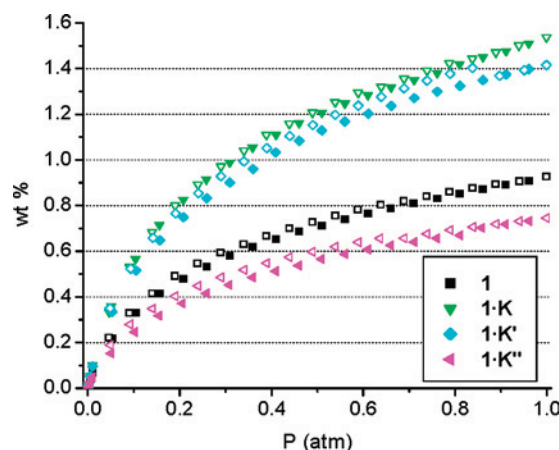
**Figure 2.** 77 K H₂ isotherms for **1** and **1•M**. Closed symbols, adsorption; open symbols, desorption.

radical anion to the diPyNI struts of **1** (see the Supporting Information). Framework reduction is reversible: upon exposure to oxygen (air), the reduced solid returns to its original color. The reduced and doped frameworks are designated **1•M**, where **M** is Li⁺, Na⁺, or K⁺.

The H₂ uptake and binding as well as structural features of the framework materials were probed by low-pressure H₂ and N₂ adsorption measurements. As we anticipated, there is a considerable increase in H₂ uptake by the reduced materials in comparison to the neutral MOF (Table 1). Low-pressure H₂ isotherms for all three **1•M**'s are shown in Figure 2. At 77 K and 1 atm, H₂ uptake increases with dopant cation size, reaching 1.54 wt % for **1•K**—a remarkable 65% (relative) increase over uptake by pure **1**.

To gain insight into the mechanism of H₂ uptake enhancement, we measured isosteric heats of H₂ adsorption, Q_{st}.¹¹ As shown in Figure 3, upon reduction and doping of **1**, we observed significant increases in Q_{st} over the entire H₂ loading range (Figure 3). Furthermore, for all three **1•M** materials, the fall off of Q_{st} with H₂ loading is shallower than that for **1**.

The ordering of average Q_{st} values, **1•Li** > **1•Na** > **1•K** > **1**, follows the cation charge-to-radius ratio, suggesting that the observed dopant-induced enhancements in heats of adsorption emanate from charge (cation)—quadrupole (H₂) interactions. Two observations, however, argue against this explanation. First, the number of extra hydrogen molecules adsorbed (at 1 atm) per dopant cation greatly exceeds the number capable of interacting directly with even a fully isolated cation (Table 1). Second, the enhancements in Q_{st} for **1•M** are much smaller than those obtained computationally

**Figure 3.** Isosteric H₂ heat of adsorption for **1** and **1•M**.**Figure 4.** H₂ isotherms at 77 K for **1•K** materials.

ally for cation-doping of solely carbon-based materials¹² or, more recently, MOFs.¹³

Additionally arguing against a dominant role for dopants as special sorption sites are the results of experiments in which the extent of doping was varied. Remarkably, as shown in Figure 4 and Table 1, increasing the amount of dopant *decreases* hydrogen uptake, ultimately to less than that for undoped **1**. (Heats of adsorption, on the other hand, are nearly identical for differentially doped samples; see the Supporting Information.) Table 1 further summarizes results for **1** doped with varying amounts of K⁺ (6, 26, and 84%; **1•K**, **1•K'**, and **1•K''**, respectively; other cations were not investigated).

Nitrogen adsorption isotherms were performed to monitor structural changes upon framework reduction and doping. All isotherms (Figure 5) display very strong uptake at low pressures, and type I behavior, indicative of microporosity. At higher pressures, however, the **1•M** isotherms exhibit

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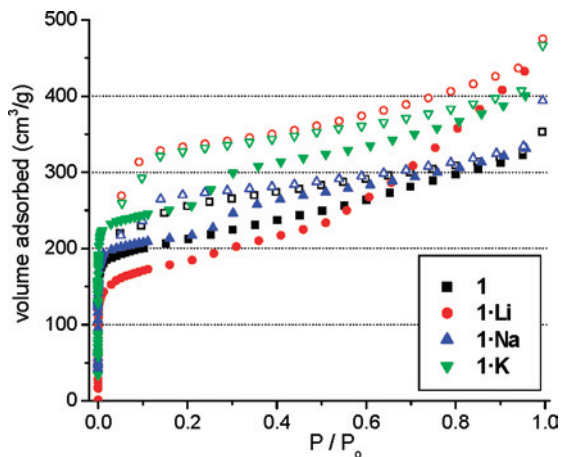


Figure 5. N₂ isotherms for **1** and **1·M**. Closed symbols, adsorption; open symbols, desorption.

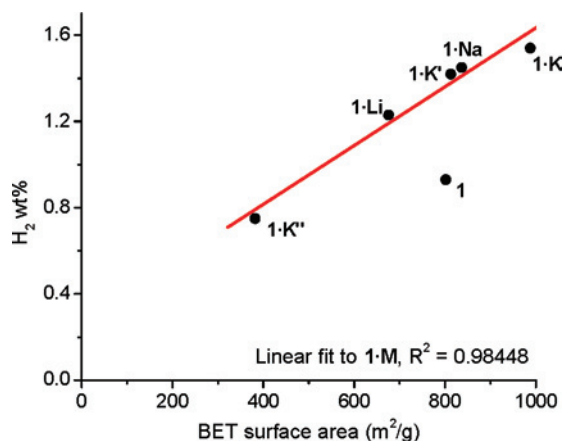


Figure 6. H₂ uptake at 1 atm plotted against BET surface area. Data for **1** is omitted in the linear fit.

stepwise adsorption and hysteresis. Furthermore, the hysteresis is repeated on subsequent adsorption/desorption cycles. We hypothesize that this unusual behavior arises from adsorbate-driven displacement of interwoven networks^{7,14} (and increase of surface area), facilitated by framework reduction and metal ion doping.

Returning to the low-pressure region, the nitrogen-accessible Brunauer–Emmett–Teller (BET) surface area, Table 1, is observed to vary substantially as a function of both dopant identity and dopant loading. Figure 6 shows that **1·M** surface areas correlate strongly with H₂ wt % uptake at 1 atm. Additionally, there exists a fair correlation between wt % uptake and micropore volume. In their computational studies, Frost and Snurr¹⁵ have emphasized that, at intermediate loading, H₂ uptake should correlate well with surface area, while at higher loading (not achieved here), uptake should correlate with micropore volume.

We suggest that the surface area variations, at low dopant levels, are largely a consequence of framework/framework displacements (recall that **1** and **1·M** are catenated materials).

The striking decreases in surface area at higher doping levels suggest that the dopant itself (K⁺) may ultimately block pores and prevent access to portions of the MOF, especially if the dopant ions retain solvent molecules. ¹H NMR measurements of the dissolved **1·K** materials, however, established that very little solvent is retained; that is, the incorporated cations are unsolvated. The measurements also established that no naphthalene is retained (see Supporting Information).

Returning to Figure 6, differences in surface area appear to account well for the differences in H₂ uptake by the various **1·M** species, but not for the differences between **1** and **1·M**; the data point for uptake for pure **1** falls considerably below the best-fit line. Table 1 indicates that differences in heats of adsorption are insufficient to explain the disparity. We suggest, following our earlier report⁷ (and the discussion above of hysteretic N₂ isotherms), that an additional consequence of framework doping and reduction is a molecular-adsorbate-driven displacement of interwoven networks. In other words, gas adsorption itself brings about further framework displacement and increases in surface area. For N₂, the increase appears to occur only at P/P_0 values above ~0.2 to 0.5 (depending on the identity of the dopant cation). Notably, these pressures are well above those used for BET fits—meaning that the BET analysis is blind to the putative “extra” surface area. In any case, the extra area may account for the additional H₂ uptake by **1·M** materials at 1 atm. In principle, variable pressure, cryogenic powder X-ray diffraction, or single-crystal X-ray structural measurements could shed light on this explanation. Unfortunately, we lack this experimental capability at present.

To summarize, framework reduction and alkali metal cation doping significantly enhance hydrogen uptake, while modestly enhancing binding. For **1**, the mechanism appears not to be the creation of special metal-based adsorption sites (as demonstrated previously at MOF corner sites)^{6,16} but instead entails favorable displacement of interwoven frameworks. The absence of large special-site effects, especially with Li⁺ as the dopant, suggests that ions may be positioned *between* frameworks and, thus, not readily accessible to H₂. Work in progress is focused on noncatenated MOFs and on divalent dopant cations, with the aim of greatly enhancing not only H₂ uptake but also the strength of MOF/H₂ interactions.

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Supporting Information Available: Full synthesis and reduction procedures, **1·K** N₂ isotherms and Q_{st} plots, 87 K H₂ isotherms of **1** and **1·M**, details of Q_{st} fit and calculations, and ¹H NMR of reduced materials. This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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