Densified HKUST-1 Monoliths as a Route to High Volumetric and Gravimetric Hydrogen Storage Capacity

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ABSTRACT: We are currently witnessing the dawn of hydrogen (H₂) economy, where H₂ will soon become a primary fuel for heating, transportation, and long-distance and long-term energy storage. Among diverse possibilities, H₂ can be stored as a pressurized gas, a cryogenic liquid, or a solid fuel via adsorption onto porous materials. Metal–organic frameworks (MOFs) have emerged as adsorbent materials with the highest theoretical H₂ storage densities on both a volumetric and gravimetric basis. However, a critical bottleneck for the use of H₂ as a transportation fuel has been the lack of densification methods capable of shaping MOFs into practical formulations while maintaining their adsorptive performance. Here, we report a high-throughput screening and deep analysis of a database of MOFs to find optimal materials, followed by the synthesis, characterization, and performance evaluation of an optimal monolithic MOF (monol MOF) for H₂ storage. After densification, this monol MOF stores 46 g L⁻¹ H₂ at 50 bar and 77 K and delivers 41 and 42 g L⁻¹ H₂ at operating pressures of 25 and 50 bar, respectively, when deployed in a combined temperature–pressure (25–50 bar/77 K → 5 bar/160 K) swing gas delivery system. This performance represents up to an 80% reduction in the operating pressure requirements for delivering H₂ gas when compared with benchmark materials and an 83% reduction compared to compressed H₂ gas. Our findings represent a substantial step forward in the application of high-density materials for volumetric H₂ storage applications.

INTRODUCTION

We are currently living in a time of great change as global transport transitions away from fossil fuels. As an alternative, H₂ gas has long held great promise as a sustainable energy vector and an automotive transportation fuel as part of the H₂ economy.¹−³ H₂ gas is a clean, potentially green, and non-toxic renewable fuel that contains much greater chemical energy per mass (142 MJ kg⁻¹) when compared to hydrocarbon fuels. The combustion of H₂ releases only water vapor as a by-product, allowing H₂ fuel cell vehicles (FCV) to potentially provide zero-emission transportation. While containing ca. three times more energy per unit mass than gasoline, its onboard storage presents significant challenges. H₂ is a very light gas and displays weak H₂...H₂ intermolecular forces, thus requiring cryogenic cooling and/or compression for storage at quantities (>5.6 kg) deemed sufficient for driving ranges (ca. 300 miles) comparable to traditional fuels.⁴

The US Department of Energy (DOE) set ambitious targets for FCV onboard H₂ storage, requiring an initial system (including tank and materials) delivery capacity of 30 g L⁻¹ (4.5 wt %) and an ultimate target of 50 g L⁻¹ (6.5 wt %). FCVs utilizing compressed H₂ gas (CHG) and cryo-compression methods have already been produced by major automobile manufacturers (BMW, Toyota, and Honda). However, these vehicles still require high gas operating pressures (>350 bar) and costly carbon fiber-reinforced storage tanks. Adsorbed gas storage (AGS) is considered a viable alternative to cryogenic or compressive storage, utilizing nanoporous materials to boost the hydrogen density in a tank at reduced operating pressures (ca. 100 bar). While traditional nanoporous materials such as activated carbons have been widely studied for H₂ storage, these materials lack the versatility and structural tunability to be considered viable options for AGS technologies.⁵−⁷

As an alternative, metal–organic frameworks (MOFs) are a class of nanoporous materials with a great potential for gas storage and separation applications. The tunability of this class of materials has given way to the synthesis of over 100,000...
reported structures with a large array of interesting properties in terms of chemical and structural diversity.\textsuperscript{8,9} This versatility of MOFs has made them widely studied for AGS applications, including H\textsubscript{2} and CH\textsubscript{4}. Several high-surface-area MOFs display benchmark performance with impressive gravimetric and volumetric H\textsubscript{2} storage densities, both on the materials and system-based levels.\textsuperscript{9} Despite these advances, two major issues need to be addressed before MOFs can be deployed in FCVs. First, MOFs generally display type I isotherms for the adsorption of H\textsubscript{2} under cryogenic conditions (Figure 1), with very high loadings at low pressures, followed by a saturation of the H\textsubscript{2} uptake at higher pressures. This limits the overall working capacity of the adsorbent materials. To address this issue, the DOE Hydrogen Storage Engineering Center of Excellence (HSECoE) has proposed designing tanks for cryoadsorption storage that operate with H\textsubscript{2} loading occurring at 77 K and 100 bar and discharge occurring at 160 K and 5 bar, ensuring that the amount of deliverable H\textsubscript{2} in nanoporous MOFs is maximized (Figure 1).\textsuperscript{10}

The second, and arguably more important, issue hampering the deployment of MOFs for gas storage applications is the shaping and densification of MOF materials. While many MOFs display exceptional gravimetric H\textsubscript{2} adsorption capacity, their performance does not readily translate to volumetric performance due to issues relating to MOF densification. MOFs are traditionally synthesized as powders with very low packing density that are formulated into shaped bodies via mechanical processes.\textsuperscript{11–13} These processes often yield low-density final products or materials with reduced performance as a result of the low pressures used in the processing or structural collapse when the pressures are high.\textsuperscript{12,14} Despite its importance, this is an area of research that has received relatively low attention, with many researchers choosing to report volumetric values based upon theoretical crystal densities as opposed to experimental bulk densities.\textsuperscript{15} While theoretical crystal densities play an important role in identifying candidate materials for H\textsubscript{2} storage, the final packing densities of shaped materials can often be only a fraction of the theoretical crystal densities. Indeed, many MOFs suffer significant losses in porosity and overall adsorption performance upon densification due to pore collapse.\textsuperscript{12,16,17} As an alternative to the densification of bulk powders, control of particle size, morphology, and monodispersity before densification has recently shown potential for improving the packing densities for MOFs.\textsuperscript{18}

In this work, we first used high-throughput computational screening and principal component analysis (PCA) to evaluate the landscape of the properties required to optimize hydrogen uptake in MOFs and to find an optimal structure, HKUST-1. Then, we used our recent developments in advanced sol–gel synthesis, engineering, and densification of MOFs to produce a pure monolithic HKUST-1 (mono-HKUST-1) structure of up to about 1 cm\textsuperscript{3} in size without using high pressures or additional binders.\textsuperscript{17,19–21} We subsequently examined the unique nature of the local structures of the high-density mono-HKUST-1 material using advanced characterization techniques such as synchrotron X-ray total scattering, mapping pair distribution function (PDF) studies, Raman microscopy, and solid-state nuclear magnetic resonance (NMR) spectroscopy studies. Finally, we examined the exceptional adsorption performance of mono-HKUST-1 as the top-performing densified MOF for volumetric H\textsubscript{2} storage. The performance of mono-HKUST-1 suggests that advanced monolithic MOFs could pave the way for a new generation of high-performance, high-density adsorbents for both onboard vehicular AGS and stationary applications, dramatically reducing the pressure requirements for onboard H\textsubscript{2} storage while improving both vehicle safety and driving distances in support of the H\textsubscript{2} economy.

## RESULTS AND DISCUSSION

### High-Throughput Computational Screening of MOFs.

The exceptional tunability of MOFs has led to the experimental synthesis of thousands of MOFs and the prediction of millions.\textsuperscript{8,22} To evaluate the landscape of MOFs in hydrogen storage in this vast chemical space, we conducted high-throughput screening (HTS) studies by performing grand canonical Monte Carlo (GCMC) simulations on a database of 2,932 experimentally synthesized MOFs at four pressures of 5, 25, 50, and 100 bar and five temperature of 77, 160, 198, 233, and 298 K. We went one step further by performing a PCA on the vast amount of data generated in the HTS studies. We also highlighted 10 benchmark MOF materials for hydrogen storage in our screening—HKUST-1, MOF-5, NU-100/PCN-100, NU-1501-Al, NU-1500-Al, Ni(dobdc), MIL-101, IRMOF-10, UMCM-9, and IRMOF-20. Although some previous HTS

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**Figure 1.** Idealized H\textsubscript{2} adsorption isotherms for FCV storage systems. Illustration of usable volumetric capacity for (a) pressure swing and (b) temperature—pressure swing storage systems. Total volumetric adsorption isotherms are shown as purple and red curves, corresponding to high and low temperatures, respectively. The “charged” state of the tank is represented by a gold star, and the “discharged” state is represented by gold diamonds. Double-sided arrows represent volumetric usable capacities achieved for each system, with \( P_{ads} = 100 \) bar and \( P_{des} = 5 \) bar.
studies have been reported in the literature, none have explored the range of conditions considered here.\textsuperscript{23−25} Figure 2a shows the general landscape of the gravimetric and volumetric surface areas of the MOFs studied here. Benchmark MOF materials such as MOF-5, IRMOF-20, and NU-1500-Al displayed both exceptional gravimetric and volumetric surface areas. While materials such as NU-1501-Al and NU-100 displayed high gravimetric surface areas, the denser structure of HKUST-1 gave way to a higher volumetric surface area. On top of that, for hydrogen tank storage, an ideal MOF structure should not only have a high hydrogen storage capacity but, more importantly, should also possess a high deliverable capacity.\textsuperscript{15}

To further probe the gas storage/adsorption performance, we determined the theoretical H\textsubscript{2} deliverable capacities of the studied MOFs under five different combined temperature−pressure swing gas delivery systems, ranging from purely cryogenic (25, 50, and 100 bar/77 K → 5 bar/160 K) to near-ambient H\textsubscript{2} delivery (100 bar/198 K → 5 bar/298 K). Figure 2b−f show the gravimetric and volumetric H\textsubscript{2} deliverable capacities; the raw data are available in a dynamic visualization tool at: https://aam.ceb.cam.ac.uk/mofexplorer.html. Part 1 of the tool contains the data for purely cryogenic H\textsubscript{2} delivery, whereas part 2 contains the data for near-ambient H\textsubscript{2} delivery. Under cryogenic conditions and high pressure (100 bar/77 K), benchmark MOFs such as MOF-5, IRMOF-20, NU-1500-Al, IRMOF-10, and NU-1501-Al get the highest values in terms of both gravimetric and volumetric deliverable capacity (Figure 2b). Interestingly, as the storage pressure decreases (Figure 2c,d), denser MOFs with open-metal sites such as HKUST-1 and Ni(dobdc) begin to match and outperform large gravimetric surface area materials under volumetric conditions; the deliverable capacities of H\textsubscript{2} for HKUST-1 display ca. 10% reduction when the storage pressure is reduced from 100 to 25 bar at 77 K. Under near-ambient conditions, HKUST-1 and Ni\textsubscript{2}(dobdc) outperformed all the other benchmark materials in terms of volumetric deliverable capacity. The exceptional performance of HKUST-1 and Ni\textsubscript{2}(dobdc) can be attributed to the denser crystal structure and high density of unsaturated metal centers, which give way to enhanced adsorbate−adsorbent interactions. The results of the HTS suggest that higher surface areas and larger pore volumes give way to exceptional H\textsubscript{2} deliverable capacities at low temperatures and high pressures. Conversely, and as expected, denser structures and stronger adsorbent−adsorbate interactions give way to enhanced H\textsubscript{2} deliverable capacities at lower pressures and higher temperatures.\textsuperscript{12,23,26}

Once the HTS data have been collected, we moved to a PCA. Commonly used for dimensionality reduction, PCA helps to choose the minimum number of variables needed to explain the maximum amount of variance in the dataset. The raw data for the PCA are available in the dynamic PCA visualization tool at https://hydrogen-storage-pca.herokuapp.com. The Supporting Information (Figures S8−S10 and Table S7) provides more details about the geometric properties’ calculation, HTS studies, and PCA. From these studies, it is clear that optimizing the density of the material along with...
selecting an appropriate adsorption pressure for the process is crucial. Indeed, while it is clear that densification is key for the deployment of MOFs, it is also well known that the excess capacity reaches a maximum and then declines with increasing pressure because it becomes more efficient to pack molecules in the gas phase than on the surface.  

**Synthesis and Characterization.** Based on the HTS and PCA, we selected HKUST-1. Not only is it a predicted volumetric absolute and deliverable capacities high but also looking at industrial production, it is based on a commercially available organic ligand and a simple synthesis process. In addition to standard synthetic methods, HKUST-1 can be made through spray-drying and mechanosynthesis. Here, we performed the synthesis of HKUST-1 not as a powder but as a high-density HKUST-1 using the previously reported sol–gel method. After the formation of the crystalline primary MOF particles at the beginning of the reaction, the mother solution was centrifuged, and the resulting MOF gel was washed to remove unreacted precursors. After three washing steps, the MOF gel was then allowed to dry overnight at room temperature, resulting in the formation of mono-HKUST-1. Figure 3a displays an optical image of mono-HKUST-1, while Figure S1 displays the powder X-ray diffraction (PXRD) patterns of the material. Once the mono-HKUST-1 was dry, activation was carried out by heating HKUST-1 to 120°C under vacuum for 12 h. The mono-HKUST-1 retains the macroscopic monolithic morphology and shape of the mold after activation. We obtained the envelope and particle packing densities of the monolithic and powdered materials, respectively, by mercury intrusion porosimetry (Figure S26).

The measured envelope density of mono-HKUST-1 is in agreement with the previously reported data, with an overall density of 1.07 g cm$^{-3}$ and verified by Particle Authority as a part of NREL H$_2$ capacity characterization. We then evaluated the porosity using N$_2$ adsorption at 77 K (Figures 3b, S2, and S3). Table S19 compares the densities, gravimetric and volumetric Brunauer, Emmett, and Teller (BET) areas calculated using Rouquerol’s updated criteria implemented in BETSI (Figures S4 and S5), and pore volumes of mono-HKUST-1 with those of powder and densified benchmark MOF materials. While mono-HKUST-1 displays one of the lowest observed gravimetric BET areas (1552 m$^2$ g$^{-1}$) and total pore volume (0.634 cm$^3$ g$^{-1}$) of the materials presented, the critical advantage of the monolithic MOF is the high bulk density, which enables benchmark volumetric performance (BET area = 1,651 m$^2$ cm$^{-3}$; pore volume = 0.675 cm$^3$ cm$^{-3}$) which far exceeds that of powdered and mechanically pressed MOF counterparts (Table S19 and Figure S46). The measured bulk density of mono-HKUST-1 (1.07 g cm$^{-3}$) is higher than the crystal densities of HKUST-1 (0.883 g cm$^{-3}$), which can be attributed to the presence of amorphous, denser phases within the monolithic material. Similar observations of high bulk density retention leading to high microporosity have been seen for previously studied mono-ZIF-8 and mono-Uio-66.  

Aiming to see if there are any structural or chemical differences between the powder and monolithic materials, we first examined the local environment of mono-HKUST-1 by NMR spectroscopy. The $^{13}$C NMR spectra (Figure 3c) for mono-HKUST-1 and HKUST-1 powder show similar peak assignments (Table S18) to those previously reported in the literature for HKUST-1, with no additional local environments observed for the BTC$^{3-}$ linker (BTC$^{3-}$ = 1,3,5-benzenetricarboxylate) in any sample. These results suggest, therefore, that the local chemical environment of the linker molecule in the powder and monolithic materials is very similar at the bulk level. To further examine the local environment, we analyzed mono-HKUST-1 by Raman microscopy. Raman spectra...
Interestingly, while the particles for both monolithic and powdered HKUST-1 were initially collected by focusing on two independent regions of the monolithic sample corresponding to the lighter and darker blue sections, respectively, as seen by optical microscopy (Figures 3d and S33–S35); Figure S36 shows the Raman spectra for both sections. The dark blue regions display a spectrum that was found to be similar to previous reports on HKUST-1, whereas the lighter blue region contains additional peaks that can be attributed to BTC hydrolytic decomposition of HKUST-1, found to contain two broader distributions, with particles of ca. 24 to 92 nm in diameter. To evaluate the uniformity of the monolith, we sectioned monolithic samples into 1 mm segments (Figure S27) and mapped them in two dimensions with 500 μm² resolution (Figure 4a). Diffraction patterns revealed differences in the scattering data collected from probe volumes at the external surface of the monolith (Figure 4b,c). To compare the relative presence of impurities, the normalized integral intensity of the spurious diffraction peak at Q ≈ 0.83 Å⁻¹ and the (222) peak (Q = 0.57 Å⁻¹) of HKUST-1 was fitted using the cumulative trapezoid method as implemented in the Python package scipy.integrate (Figure 4e–h). To further probe the monolithic HKUST-1 PDF, we analyzed the data using previously described non-negative matrix factorization (NMF) techniques. Two components were used to describe the data (Figures 4d,i–l and S29). Comparison of these maps (Figure S30) reveals reasonable corroboration between the PDF-NMF components and the spurious diffraction peaks observed, with component A having a mean Pearson correlation of 0.92 with the (222) peak of slice 1 and 0.98 with the (222) peak of slice 2, and component B having a mean Pearson correlation of 0.78 with the spurious peak of slice 1 and 0.91 with the spurious peak of slice 2. Diffractograms collected in this region included additional peaks consistent with those previously ascribed to the hydrolytic decomposition of HKUST-1 (Figure 4i). In contrast, the center of the monolith samples exhibited little to no presence of these peaks (Figure 4j) and fitted well with an HKUST-1 model without evidence of impurities. Indeed, this mapping matches with an observed difference in color between the center (dark blue) and edge (light blue) of the sample. Taking into account the above observations on Raman scattering, this further suggests the existence of HKUST-1 and a hydrated form, respectively. An analysis of the PDF data decomposed the data into two phases that correlate well with the distribution of HKUST-1 and the additional diffraction peaks. The PDF component corresponding to additional diffraction peaks exhibits limited radial distance atom–atom correlations with the exception of an increase in Cu–Cu distances, consistent with the hydration of the paddlewheel (Figure S30). It is remarkable that densification of the material in monolithic HKUST-1 not only improves volumetric adsorption but may also improve the hydrolytic stability of the material by limiting accessible surfaces to the outer edges of the monolith. The hydration of the Cu paddlewheels on the outer surfaces of HKUST-1 may act in a “sacrificial” manner similar to that observed for STAM-17-OEt, enabling the retention of the bulk porosity upon exposure to moisture. This was confirmed using 77 K N₂ adsorption isotherms, which were performed on...
a mono HKUST-1 sample stored at room temperature for 18 months. This sample was found to retain over 90% of its overall BET area and porosity after 18 months of storage (Figure S48). The monolithic nature was found to significantly improve the chemical stability of the mono HKUST-1 material.

Hydrogen Storage Performance. To probe the improved performance of densified MOFs in H\textsubscript{2} storage, we collected high-pressure adsorption isotherms at eight temperatures from 75.6 to 303 K and up to 140 bar (Figures 5 and S12−S15) on mono HKUST-1. To ensure reproducibility of the data, this was done in three separate laboratories: NREL, the University of Alicante, and the University of Cambridge. It is important to note that the experimentally measured values are excess amounts adsorbed (\(N_{\text{exc}}\)), which were then transformed into absolute uptakes (\(N_{\text{abs}}\)) by using eq 1 (Supporting Information, eq 5)

\[
N_{\text{abs}} = N_{\text{exc}} + \rho V_{\text{pore}}
\]

where \(\rho\) is the density of the gas at the given adsorption pressure and temperature, obtained from the National Institute of Standards and Technology (NIST),\textsuperscript{37} and \(V_{\text{pore}}\) is the pore volume of the adsorbent.\textsuperscript{27} The calculated absolute adsorption (\(N_{\text{abs}}\)) (Supporting Information, eq 5) based on excess (\(N_{\text{exc}}\)) H\textsubscript{2} isotherms collected at 75.6, 77, and 77 K (Figures S1a, S14, and S15) at NREL, the University of Cambridge, and the University of Alicante, respectively, were found to be in good agreement, displaying similar H\textsubscript{2} uptakes at corresponding pressures for each of the three isotherms. Figures S12 and S13 display the NREL excess and calculate total (\(N_{\text{abs}}\)) (Supporting Information, eq 6) H\textsubscript{2} uptake at 75.6 and 303 K for comparison.\textsuperscript{38−40} Figure 5b shows the absolute (\(N_{\text{abs}}\)) volumetric adsorption isotherms of H\textsubscript{2} at 75.6 K in mono HKUST-1 compared with a densified HKUST-1 powder and a simulated H\textsubscript{2} isotherm for HKUST-1. The difference between isotherms is striking; interestingly mono HKUST-1 displays higher H\textsubscript{2} uptake at lower pressures compared to the densified powder sample, achieving a saturation uptake of ca. 46 g L\textsuperscript{-1} at 50 bar. In comparison, the densified HKUST-1 powder achieves an uptake of only ca. 28 g L\textsuperscript{-1} at 50 bar and of ca. 38 g L\textsuperscript{-1} at 100 bar. In comparison, the simulated absolute H\textsubscript{2} uptake of HKUST-1 (ca. 45 g L\textsuperscript{-1}) and mono HKUST-1 isotherms displays similar features. The higher uptake of mono HKUST-1 compared to the simulated isotherm can be attributed to the envelope density observed in mono HKUST-1 (1.07 g cm\textsuperscript{-3}), which exceeds the theoretical crystal density for HKUST-1 (0.883 g cm\textsuperscript{-3}).

Figure 5c compares the volumetric H\textsubscript{2} adsorption performance of mono HKUST-1 with the performance of previously reported densified MOF materials (Figure S41) using real bulk densities of the materials;\textsuperscript{12,13,31,41−44} Figure S40 compares the performance of mono HKUST-1 with the performance of previously reported benchmark MOF materials, with the caveat that this is done based on theoretical single-crystal density.\textsuperscript{12,24,25,45,46} Typically, a densified polycrystalline powder, as described above, will be many times limited to a density 50% lower than the theoretical crystal density.\textsuperscript{12,16}
Importantly, a recent report has shown that the precise control of the MOF particle’s shape and size can give way to improved bulk densities in shaped MOF materials. Although the gravimetric $\text{H}_2$ uptake of mono-HKUST-1 is lower than that of all the previously reported materials studied herein (Table S19), the mono-HKUST-1 material displays benchmark volumetric $\text{H}_2$ adsorption performance. The closest material to mono-HKUST-1 in terms of performance is MOF-5, displaying a $\text{H}_2$ adsorption capacity of ca. 43 g L$^{-1}$ at 100 bar. The performance of mono-HKUST-1 was also found to outperform the benchmark carbon-based material AX21 at 100 bar and 77 K (Table S19). The $\text{H}_2$ uptake performance of mono-HKUST-1 at 25 and 50 bar exceeds the 100 bar uptake of the densified powder MOFs (Table S19, Figures S5c and S42). The exceptional performance of the mono-HKUST-1 sample is attributed to the high bulk density achieved via a sol–gel synthesis approach, overcoming the lower densities and mechanical degradation issues associated with traditional powder pressing techniques.

The effects of mechanical pressing of MOFs have a detrimental impact on the overall $\text{H}_2$ adsorption performance for storage applications. For conformed, pressed polycrystalline powder materials, typical $\text{H}_2$ excess adsorption capacities are generally retained up to a point where the density is increased up to ca. 50% of the single-crystal density (Figure S47). After that point, although the density continues to increase, the maximum excess adsorption value starts to decrease due to the continued mechanical collapse of the MOF. In contrast, the mono-HKUST-1 sample was found to retain a high $\text{H}_2$ adsorption capacity at bulk densities exceeding those of the crystal density of HKUST-1 (i.e., 1.07 vs 0.883 g cm$^{-3}$). As has been seen elsewhere, the high-pressure $\text{H}_2$ adsorption performance of the densified MOFs was found to follow a similar trend to that of the volumetric BET areas of the materials studied (Figure S5d). This means that volumetric BET area, using an appropriate density, is a valuable descriptor to predict the volumetric performance of MOFs.

To determine the adsorbate–adsorbent interaction energies for mono-HKUST-1, we calculated the isosteric heats of adsorption ($Q_{st}$) from $\text{H}_2$ isotherms collected at eight temperatures using the Virial method (Figures S38 and S39). The experimental $Q_{st}$ value for mono-HKUST-1 was found to be in the range of 3.7–5.5 kJ mol$^{-1}$. This value was found to be consistent with previously reported values for HKUST-1 in addition to other benchmark copper paddlewheel MOFs (NOTT-112 and NU-125). $Q_{st}$ is an important variable in understanding how easy it is to release the gases at lower pressures and/or higher temperatures. Indeed, the storage and release temperatures are another key factor for $\text{H}_2$ storage materials. Since the current DOE targets only address hydrogen delivery temperature (−40 to 85 °C, to meet fuel cell system operation specifications) and not the storage system operating temperature, a range of possible system designs can be considered. To assess the performance of mono-HKUST-1 over a wide range of temperatures, we applied the dual-process Langmuir (DPL) equation to the experimental isotherms (Figures S16–S25). We found the DPL equation to be in good agreement with the experimental data collected at eight temperatures. The initial conditions assessed for storage of $\text{H}_2$ were near ambient (−75 to 100 °C) up to 100 bar (Figure 6a and Table S21). Mono-HKUST-1 displays a $\text{H}_2$ adsorption capacity of 10.1 g L$^{-1}$ at 25 °C and 100 bar, which is, to the best of our knowledge, the highest measured $\text{H}_2$ capacity of a densified MOF—using real MOF density—under these conditions. However, the usable capacity in this case, with no temperature swing, is slightly reduced to 9.3 g L$^{-1}$ due to the uptake of 0.84 g L$^{-1}$ at 5 bar. This still outperforms compressed hydrogen, which would require compression to over 150 bar to obtain the same total volumetric usable capacity at 25 °C (Figure 6b). At 100 bar and a temperature of −75 °C, mono-HKUST-1 takes up a total of 16.5 g L$^{-1} \text{H}_2$, which corresponds to a total usable capacity of 14.8 g L$^{-1}$. If the use of a temperature swing in a storage system is considered, through the application of active cooling at high filling levels, the usable capacities attained with mono-HKUST-1 are even higher. For example, adsorption at −40 °C and desorption at 25 °C afford a usable capacity of 12.4 g L$^{-1}$. A temperature swing from adsorption at −75 °C to desorption at 25 °C gives a usable capacity of 15.7 g L$^{-1}$. This usable capacity represents the highest $\text{H}_2$ volumetric usable capacity achieved to date for a densified adsorbent operating in this temperature range. Although these values are comparable to the current theoretical benchmarks (Ni$_2$(dobdc), MOF-5, and V$_2$Cl$_8$(btdd)) under these conditions (Table S21), it is important to highlight that these previous values are based on theoretical crystal densities and not experimental envelope densities, as reported here for mono-HKUST-1. A natural assumption is to expect a ca. 50% reduction in the density and therefore in volumetric capacities in densified powders.

When cryogenic conditions are employed for $\text{H}_2$ storage, the use of a temperature swing step (i.e., 77 to 160 K) can increase the usable capacities by increasing the quantity of $\text{H}_2$ desorbed upon cycling. While mono-HKUST-1 displays an overall $\text{H}_2$ adsorption performance...
uptake of 46.0 g L\(^{-1}\) at 100 bar and 77 K, the high H\(_2\) uptake at low pressures limits the working capacity to 11.2 g L\(^{-1}\). When a combined temperature—pressure swing system (100 bar/77 K → 5 bar/160 K) is employed, the working capacity increases to 43.3 g L\(^{-1}\) (Figure 6c). This exceeds the performance of all densified MOF benchmarks under similar conditions (Table S20). Although, a priori, this may sound contrary to the results obtained from the HTS, here it is important to point out that the force fields used in simulations tend to under-predict the H\(_2\) uptake for MOFs containing open-metal sites—including benchmark MOFs such as HKUST-1, NU-100, Ni(dobdc), and MIL-101 considered in this study—particularly at low pressures where polarization can play a significant role in H\(_2\) adsorption. Also, the structures used in silico are perfect single crystals and do not contain defects such as missing linkers, missing clusters, and so forth commonly seen in experimental structures. Combined, this can lead to differences between experimentally determined and theoretically delivered capacities. Interestingly, the \(\text{mono}_{\text{HKUST-1}}\) sample reaches >95% (43.8 g L\(^{-1}\)) saturation at 25 bar, enabling H\(_2\) saturation at much lower pressures compared to many benchmark MOFs. When lower adsorption pressures are taken into account (Figure 6d), \(\text{mono}_{\text{HKUST-1}}\) exhibits working capacities of 42.3 and 40.5 g L\(^{-1}\), for loading pressures of 50 (50 bar/77 K → 5 bar/160 K) and 25 bar (25 bar/77 K → 5 bar/160 K), respectively. These values represent a 302 and 119% increase in the \(\text{H}_2\) volumetric storage capacities of an empty tank at 25 and 50 bar, respectively. By comparison, under ambient temperatures, H\(_2\) gas would need to be pressurized to 145 and 700 bar at 77 and 298 K, respectively, to achieve similar storage capacities. Again, to the best of our knowledge, this is the highest deliverable capacity achieved by any adsorbent after successful pelletization and shaping.

To design a material for adsorption applications, its volumetric capacity is not the only parameter that needs to be taken into consideration. Looking at the DOE targets, heat management due to the exo/endothermic nature of the adsorption/desorption phenomena, as well as efficient packing of a monolith in a tank, impurity tolerance (e.g., CO, H\(_2\)O), recyclability (e.g., 100 cycles), and cost of adsorbent need to be optimized. In the case of \(\text{mono}_{\text{HKUST-1}}\), the three times higher density compared with that of the powder is expected to improve heat transfer significantly. Moreover, the generic approach of the sol–gel synthesis also allows for doping with materials such as activated carbon with higher thermal conductivity. In terms of cost, the primary limiting factors for \(\text{mono}_{\text{HKUST-1}}\) production include the starting materials’ cost, high solvent usage, and centrifuge cycling times. Solvent reduction and recovery combined can massively reduce \(\text{mono}_{\text{HKUST-1}}\) production costs (Figure S50). Additionally, by employing liquid-assisted grinding, it is possible to significantly reduce mixing times by using prepared nanocrystalline powders to form high-density \(\text{mono}_{\text{HKUST-1}}\) materials while maintaining monolith quality (Figure S49). Predictably, yield is also a large cost driver, and any cost-effective production will seek to maximize yield. The simplicity of the synthesis of monolithic MOFs combined with their exceptional performance indicates that monolithic MOFs could play an important role in fuel gas storage in the coming decades.

## CONCLUSIONS

In conclusion, we have investigated computationally the landscape of MOFs for H\(_2\) storage and selected HKUST-1 as the optimal structure due to its adsorption capacity and ease of synthesis. Following this, we synthesized and analyzed the structure and H\(_2\) adsorption properties of the monolithic version, \(\text{mono}_{\text{HKUST-1}}\). SAXS, NMR spectroscopy, and Raman microscopy studies demonstrated that \(\text{mono}_{\text{HKUST-1}}\) exhibits similar characteristics in terms of composition and connectivity to powdered HKUST-1. However, the small and uniform primary particles result in exceptionally close packing, giving way to high-density final materials when mild drying conditions are applied. The monolithic structure of \(\text{mono}_{\text{HKUST-1}}\) also gives way to reduced material degradation, a common issue with HKUST-1 powders. The high-density structure forms an oxidized layer on the external surface which reduces the exposure of HKUST-1 particles within the monolith to moisture, maintaining exceptional performance after prolonged periods of exposure to the atmosphere. The exceptional high-density structure of \(\text{mono}_{\text{HKUST-1}}\) enables the formation of materials that maintain porosity after shaping and display benchmark volumetric BET areas, which in turn gives way to exceptional H\(_2\) sorption performance. The \(\text{mono}_{\text{HKUST-1}}\) materials were found to be capable of achieving H\(_2\) working capacities at 25 bar under cryogenic conditions, which was only possible by compressing H\(_2\) to 700 bar at room temperature. This reduction in operating pressures has the potential to significantly reduce the systemwide engineering requirements and cost while simultaneously improving the overall safety of onboard H\(_2\) storage for vehicular transport. While further development is required to identify more stable materials with high working capacities, this work represents a significant step forward in the shaping and densification of MOFs for H\(_2\) storage applications.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c04608.

Additional experimental procedures, in situ procedures and results, and computational information (PDF)

Full details of previous high-throughput screening (HTS) studies of MOFs for H\(_2\) storage (XLSX)

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Notes

The authors declare the following competing financial interest(s): David Fairen-Jiménez has a financial interest in the start-up company Immaterial Ltd., which is seeking to commercialize metalorganic frameworks.

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