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May 26, 2009

Journal of the American Chemical Society
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Metal organic frameworks as templates for nanoscale NaAlH₄
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Hydrogen has many of the properties of an ideal energy carrier, its storage remains a key problem in the development of an economy based on this fuel.¹ Metal hydrides are the focus of intensive research for vehicular storage.² In addition to significant volumetric and gravimetric constraints imposed by this application, in the case of on-board rehydrogenation it is also necessary that this be feasible at temperatures produced by waste heat from a fuel cell-driven power train. Although light-metal hydrides in some cases meet the gravimetric and volumetric capacity requirements, they have two distinct disadvantages which inhibit their use in on-board reversible storage applications. First, their chemical bonds are often strong, resulting in high thermodynamic stability and low equilibrium hydrogen pressures. Second, the directionality of the covalent/ionic bonds in these systems leads to large activation barriers for atomic motion, resulting in slow hydrogen sorption kinetics and limited reversibility.³ Although concepts such as hydride destabilization by the use of additives,⁴ doping⁵ or alloying,⁶ and kinetic enhancements using catalysts⁷ have been intensively investigated, to date these strategies have not allowed hydrides with the highest weight and volumetric capacities to be used.

Recently, theoretical and experimental evidence suggest that reducing hydrides from the bulk state to a critical dimension on the nanoscale could address both the thermodynamic and kinetic limitations inherent in bulk light-metal hydrides.¹ However, the magnitude and direction of the effect, as well as the critical length at which these effects occur, are unclear. Quantum-chemistry modeling suggests that the H₂ desorption energy is less than bulk for (MgH₂)n (n < 10 Mg atoms) are thermodynamically destabilized.² However, a Wolf-construction model predicts that the effect is hydride-specific, with only MgH₂ and NaH destabilized at the nanoscale.²⁰ Experimental data are promising but disagree with theory. Mechanical ball milling has been widely used, but this method is fraught with problems, including impurity inclusions, lack of size control, and poor reproducibility. In an attempt to control size more effectively, carbon aerogels, carbon nanofibers, and ordered mesoporous silica have been used as templates and infiltrated with NaAlH₄,³⁵ MgH₂,³⁵ and LiBH₄.³⁵ Enhanced dehydrogenation kinetics compared to bulk materials are observed,³⁵ but the wide distribution of pore sizes yields non monodisperse particle sizes ranging from 2 nm to 10 μm, making a clear assignment of the destabilization mechanism impossible.³⁵ There also is evidence that the chemical environment surrounding the particle plays a role. Catalytic surface effects are predicted in carbon-based templates and improved desorption kinetics of relatively large (5 nm) colloidal MgH₂ particles also suggest that nanoscale effects are not solely result of reduced particle size. Since the myriad of possibilities inhibits progress toward development of an effective storage material, it is clear that a new synthetic platform must be developed that provides control over both particle size and local environment so that the root causes of nanoscale effects can be established.

In this work, we demonstrate that metal organic frameworks (MOFs) are effective templates for the synthesis of nanoscale metal hydride particles and that infiltration leads to considerably accelerated H₂ desorption kinetics for NaAlH₄. Furthermore, in contrast with the disordered templates such as carbon nanofibers, MOFs provide a highly controlled and inherently understandable environment for probing phenomena associated with nanoscale such materials. The permanent nanoporosity of MOFs, which is created by a crystalline (and therefore ordered) lattice, provides the ability to systematically tailor pore shape, size, and chemistry without complications from broad pore-size distributions or difficult-to-characterize surface chemistry.

We selected HKUST-1 (Cu₆(BTC)₄) as a template for detailed investigation (BTC = Benzene tricarboxylic acid) because its pore openings are much smaller than the interior dimensions, which should limit nanoparticle mobility (4 pores/unit cell with 9 Å x 9 Å openings and 11 Å x 16 Å interior dimensions).³⁸ A second set of pores (8/unit cell) are even smaller (XÅ x XÅ), but are almost completely inaccessible to the THF solvent used here. HKUST-1 is also reported to be thermally stable up to 250 °C, enabling H₂ desorption from several hydrides without MOF decomposition.³¹

![Figure 1](image-url)
We also evaluated the potential of IRMOF-1 and MIL-68 for use as hydride templates. We infiltrated dehydrated Cu₃(BTC)₂ MOF³ with a solution of NaAlH₄ in THF to allow comparisons with infiltrated carbon nanofibers.⁴ The infiltrated material 1 was washed with THF and heated to 110 °C under vacuum to remove guest solvent, yielding 2, which has 3.9 wt% NaAlH₄ by elemental analysis. From the published crystal structure we determine there are 6 THF molecules and 3 formula units of NaAlH₄ for each large Cu₃(BTC)₂ MOF pore. FTIR of 2 shows intense bands at 1653 cm⁻¹, corresponding to ν(C=O) stretching mode, and 845 cm⁻¹, corresponding to ν₅[AlH₄]⁻ bending mode.⁵ New bands in 2900-2249 cm⁻¹ region could not be definitively assigned, but may be due to THF coordinated to open coordinated sites of Cu (Fig. 1).

Powder X-ray diffraction patterns⁶ of 1 and 2 show that this MOF template is stable in the presence of NaAlH₄. No specific reflections corresponding to the infiltrated NaAlH₄ are observed in 2, indicating that the infiltrated NaAlH₄ is either amorphous or too small to be visible by XRD. This evidence, combined with the FTIR data, suggests that the hydride is uniformly distributed throughout the template.

¹H MAS NMR was performed on a variety of samples, including NaAlH₄·THF @Cu₃(BTC)₂ MOF (1), Cu₃(BTC)₂ MOF with NaAlH₄ in the absence of THF (2) (dried at 110 °C), Cu₃(BTC)₂ MOF in THF, and Cu₃(BTC)₂ MOF (3). ¹H MAS NMR spectrum on 1 shows four intense peaks at 1.72ppm, 3.58ppm, -4.63ppm, and -7.88ppm. The peaks at 1.72 and 3.58 ppm represent the physisorbed THF, which displays the same chemical shifts as liquid THF. The peaks at -4.63ppm and -7.88ppm represent THF bound to free coordination sites on the copper of the Cu₃(BTC)₂ MOF. In addition, there exists two additional peaks at 9.06ppm, which represents protons of the aromatic trimesic acid linker in the Cu₃(BTC)₂ MOF and 6.04ppm, which potentially represents protons from the MOF structure interacting with the THF. These sample peaks are also present in the spectra of 2 (dried at 110 °C). These peaks corresponding to trimesic acid protons are rather broad and of diminished intensity in case of 1 because the peaks at 1.72ppm and 3.58ppm, which are associated with free THF, saturate the broader peaks. The protons that are associated with NaAlH₄ are much broader and have a longer relaxation time. This peak is not shown in this data. However, we have seen a peak grow in with a relaxation time of 20s at 3.09ppm, which represents the proton in NaAlH₄. From the proton NMR studies, we have found that there is only approximately 10% THF left in the system. Since it is very difficult to completely remove the THF, we are currently exploring how THF affects the overall structure of the Cu₃(BTC)₂ MOF with NaAlH₄.

²⁷Al and ²³Na Magic Angle Spinning (MAS) NMR spectrum confirm the presence of NaAlH₄ inside MOF structure. The as-synthesized sample 1 exhibits a ²³Na shift at -1.8 ppm. In contrast, this signal in 2 is shifted upfield to -9.4 ppm; neat NaAlH₄ has a similar chemical shift. This indicates that the Na stays intact within the MOF structure. ²⁷Al MAS NMR of NaAlH₄·THF@Cu₃(BTC)₂ shows a narrow peak at 96.2 ppm. After the THF solvent is removed, the signal is broadened and shifted slightly upfield to 94.4 ppm. The ²⁷Al MAS NMR of pure NaAlH₄ has a chemical shift of 94.6ppm. Some Al₂O₃ impurity peaks are also observed at 8.4, 35.5 and 63.6 ppm respectively. The ²⁷Al MAS NMR can observe the level of impurities in the NaAlH₄, which in this case is less than 5%. In addition, the ²³Na and ²⁷Al MAS NMR data shows that the NaAlH₄ is completely intact within the Cu₃(BTC)₂ and is no longer interacting with the THF.

Temperature programmed experiment,⁷ in which we monitored m/z = 1 – 220, on neat NaAlH₄ clearly shows Hydrogen desorption begins at ~180 °C, corresponding to incongruent melting of the sample, with the majority of the H₂ (~ 70wt%) desorbing at ~250 °C. Subsequent desorption at ~300 °C is due to NaH. THF is strongly coordinated to the Cu sites in sample 2. So 2 is subjected to 110 °C for 10 hours at ~10⁻³ m torr, in an effort to remove the THF coordinated to the copper sites. Even with such drastic conditions, only 85% of the coordinated THF could be removed. Subsequently this sample was subjected to temperature profile shown in Fig. 2. It can be seen from Fig. 2 that confinement of NaAlH₄ within the MOF pores dramatically accelerates the desorption kinetics. Hydrogen desorption could be seen at temperatures as low as 70 °C.

³°C albeit rate of desorption is rather low. But the desorption rate increases between 130 °C – 155 °C and this temperature range constitutes ~80% of the total H₂ amount desorbed from the sample (Fig. 2). When compared to the neat NaAlH₄, this is an improvement of about 100° C in terms of desorption temperature.

The sharp desorption signal at ~180° C is attributed to incongruent melting of the NaAlH₄. Thermal decomposition of Cu₃(BTC)₂ MOF starts at 250° C, as indicated by rapid evolution of CO₂ from the sample,⁸ in accordance with published literature.⁹

Transmission electron microscopy (TEM) of 2 shows 5 – 10 nm particles. However, NaAlH₄ is known to be unstable under TEM conditions where Na and Al segregate into nanosized domains rendering the TEM imaging difficult.¹⁰ Furthermore, we find that highly focused TEM beams required to image very small particles destroy the MOF crystal structure. This happens within few seconds in the case of HKUST-1. As a result, the hydride nanoparticles coalesce into much larger particles.¹¹ This appears to
be a general problem associated with MOF templates and requires the use of other methods to establish particle size.

We conclude that MOFs can be effectively used as a nano scale templates for infiltration of NaAlH₄. Significant destabilization of nano scale NaAlH₄ was observed leading to lower desorption temperature and higher rate of release of hydrogen, compared to bulk. The significance of this study can be extended beyond NaAlH₄ and Cu₄(BTC)₂ MOF, including other complex metal hydrides and infiltrating into pores of MOFs with one, two and three dimensional channels having a variety of metal centers. By systematically varying such parameters it is possible to study whether destabilizing of metal hydrides is dictated only by size of the metal hydride clusters, its local environment in confined space, or those catalytic effects of framework metal centers.

ACKNOWLEDGMENT: This work was funded by the US Department of Energy Hydrogen, Fuel Cells, and Infrastructure Technologies Program. This work was funded by the US Department of Energy Hydrogen, Fuel Cells, and Infrastructure Technologies Program. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors thank Miles Clift for performing XRD and Prof. Eric Majzoub for helpful discussions.

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