by Ohno et al. expands the space of candidate thermoelectric materials by entering into unexplored territory.

Despite the initial success of phase boundary mapping, much more remains to be done for thermoelectric applications. Instead of only mapping out the *p*-*n* boundary on the phase diagram, eventually, mapping of physical properties, such as σ, k, or even zT, on a given phase diagram can probably be considered the ultimate goal of this approach. Given the extremely high computational cost for calculating transport properties from first principles, other approaches may be implemented to fulfill this goal, such as analytical calculations, which is particularly effective for defects.[11] Only then are we directly optimizing thermoelectric performance instead of indirectly optimizing carrier concentration. Even so, whether or not the optimized zT remains optimal after material modification is still a completely open question.

1. Zebarjadi, M., Esfarjani, K., Dresselhaus, M.S., Ren, Z.F., and Chen, G. (2012). Perspectives on thermoelectrics: from fundamentals to device applications. Energy Environ. Sci. *5*, 5147.
2. Zhang, X., and Zhao, L.-D. (2015). Thermoelectric materials: Energy conversion between heat and electricity. Journal of Materiomics *1*, 92.
3. Snyder, G.J., and Toberer, E.S. (2008). Complex thermoelectric materials. Nat. Mater. *7*, 105–114.
4. Dresselhaus, M.S., Chen, G., Tang, M.Y., Yang, R.G., Lee, H., Wang, D.Z., Ren, Z.F., Fleurial, J.P., and Gogna, P. (2007). New directions for low-dimensional thermoelectric materials. Adv. Mater. *19*, 1043.
5. Biswas, K., He, J., Blum, I.D., Wu, C.I., Hogan, T.P., Seidman, D.N., Dravid, V.P., and Kanatzidis, M.G. (2012). High-performance bulk thermoelectrics with all-scale hierarchical architectures. Nature *489*, 414–418.
6. Pei, Y., Shi, X., LaLonde, A., Wang, H., Chen, L., and Snyder, G.J. (2011). Convergence of electronic bands for high performance bulk thermoelectrics. Nature *473*, 66–69.
7. Minnich, A.J., Dresselhaus, M.S., Ren, Z.F., and Chen, G. (2009). Bulk nanostructured thermoelectric materials: current research and future prospects. Energy Environ. Sci. *2*, 466.
8. Ohno, S., Imasato, K., Anand, S., Tamaki, H., Kang, S.D., Gorai, P., Sato, H.K., Toberer, E.S., Kanno, T., and Snyder, G.J. (2018). Phase boundary mapping to obtain *n*-type Mg_3Sb_2-based thermoelectrics. Joule *2*, this issue, 141–154.
9. Tamaki, H., Sato, H.K., and Kanno, T. (2016). Isotropic conduction network and defect chemistry in Mg3+δ Sb2 -based layered Zintl compounds with high thermoelectric performance. Adv. Mater. *28*, 10182–10187.
10. Toberer, E.S., May, A.F., Melot, B.C., Flage-Larsen, E., and Snyder, G.J. (2010). Electronic structure and transport in thermoelectric compounds AZn2Sb2 (A = Sr, Ca, Yb, Eu). Dalton Trans. *39*, 1046–1054.
11. Li, M., Ding, Z., Meng, Q., Zhou, J., Zhu, Y., Liu, H., Dresselhaus, M.S., and Chen, G. (2017). Nonperturbative quantum nature of the dislocation-phonon interaction. Nano Lett. *17*, 1587–1594.

Preview

Tricking Inert Metals into Water-Absorbing MOFs

Adam J. Rieth[1] and Mircea Dincă[1,*]

In a recent issue of *Chem*, Towsif Abtab et al. describe a Cr^{3+}-based metal-organic framework (MOF) that can capture a record-shattering 200% of its weight in water. Remarkably, whereas the Fe^{3+} and Al^{3+} variants of the framework collapse upon water exposure, the Cr^{3+} version shows no decline in crystallinity or capacity after 100 cycles of water uptake. Synthesized via a cation exchange process of Cr^{2+} for Fe^{3+}, the achievement of the highly porous Cr^{3+} structure points the way toward additional MOF topologies with exceptional stability enabled by inert metals.

Initial and continued interest in metal-organic frameworks (MOFs) is in large part due to their record surface areas and porosities. Materials with superlative surface areas portend applications in many areas, foremost gas storage and separations.[1] Spurred on by these applications, in recent years researchers pursued frameworks with ever-greater pore volumes and surface areas. However, the increasing pore volume and surface area typically comes at the expense of stability, and the expanded structures often require delicate handling procedures such as airfree techniques, exclusion of water, or supercritical CO_2 activation to prevent pore collapse.[2] Now, reporting recently in *Chem*, Towsif Abtab et al. describe an exceptionally porous framework made from Cr^{3+} with a pore volume approaching 2 $cm^3\ g^{-1}$ and excellent stability.[3] Although identical structures made from Fe^{3+} or Al^{3+} collapse in the presence of water,[4] the Cr^{3+} structure is supremely stable. Coupled with the high pore volume, this leads to a record-setting water uptake capacity of nearly 200 percent by weight (wt%).[3]

MOFs are most often synthesized from labile metal ions such as Zn^{2+}, which favor reversible weak-field ligand binding to

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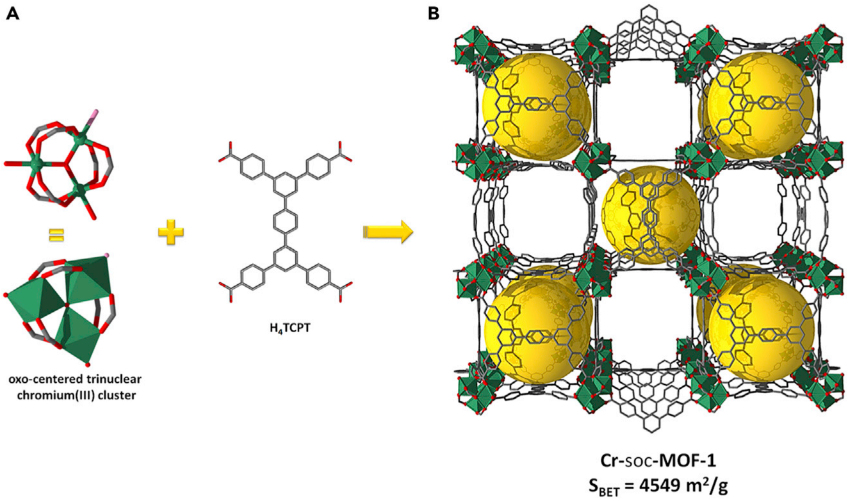

Figure 1. Structure and Composition of Cr-*soc*-MOF-1

(A and B) The framework structure of Cr-*soc*-MOF-1 (B) is made up of trinuclear chromium clusters bridged by the tetratopic carboxylate linker termed H_4TCPT (A). Cr, green; C, gray; O, red; Cl, pink. Hydrogen atoms have been omitted for clarity. Image reproduced from Towsif Abtab et al.[3]

promote thermodynamically controlled crystal growth. The formation of MOFs using inert metal ions such as Cr^{3+} is more difficult because the error-checking enabled by reversible metal-ligand bond formation is not as efficient. The synthesis of such MOFs requires harsh synthetic conditions such as high temperature and pressure, as well as the presence of mineralizers such as HF.[5] Even under these conditions, the materials form as microcrystallites whose sizes are much smaller than those of MOFs formed from labile metal ions, complicating structural investigations. Despite these challenges, MOFs made from inert metals are attractive because they may be better suited to conditions relevant for many applications, such as gas storage and separations involving impure gas streams containing water vapor, ammonia, or acid gases. The prototypical Cr-MIL-101, the previous record holder for total water uptake, is the preeminent example of an exceptionally stable MOF formed from an inert metal,[6] although the trend of inert metal ions providing increased stability is evident in numerous other examples. For instance, even partial replacement of Mg^{2+} in Mg-MOF-74 with more inert Ni^{2+} ions significantly enhances the stability of the Mg material.[7]

Towsif Abtab et al. targeted the Cr-*soc*-MOF-1 structure (Figure 1), which was expected to share the topology of MOFs previously synthesized with Al^{3+} or Fe^{3+} connected with the same tetratopic carboxylate ligand 3,3′,5,5′-tetrakis(4-carboxyphenyl)-p-terphenyl (H_4TCPT).[3,4] However, the authors were unable to obtain the desired Cr^{3+} structure from typical solvothermal conditions using Cr^{3+} and H_4TCPT. When direct synthesis of targeted MOF structures with desired metal ions proves to be impossible or leads to undesirable products, researchers often turn to cation exchange as an alternative synthetic pathway.[8] In this mild process, a framework synthesized with a native metal ion is soaked in a solution of the desired metal ion, which then replaces the cations in the parent framework. In this case, the authors synthesized the Fe^{3+} framework with the desired *soc* topology then soaked the crystals in a concentrated solution of Cr^{2+}. This led to nearly complete exchange of Fe^{3+} to Cr^{3+}. The cation metathesis likely occurs in a stepwise process in which labile Cr^{2+} ions first replace the native Fe^{3+} ions and second are oxidized to inert Cr^{3+}, "locking-in" the original *soc* topology and considerably increasing stability relative to the parent Fe material.

With the inert Cr^{3+} ions now making up the secondary building units of the MOF, the material exhibits inertness to coordinating molecules such as water. A water vapor isotherm (Figure 2) indicates a total uptake of approximately 200 wt% in a single large step near a relative humidity (RH) of 60%. The record water capacity correlates directly with the exceptional pore volume of approximately 2 $cm^3\ g^{-1}$ measured by a nitrogen adsorption isotherm. These data indicate that the MOF pores are being completely filled with water close to the density of liquid water. More fundamentally, while most materials with pore volumes of greater than 1 $cm^3\ g^{-1}$ collapse upon water uptake due to capillary condensation forces, the exceptional stability to water uptake, with no change in the water isotherm after 100 cycles (Figure 2), indicates that the incorporation of the inert Cr^{3+} ion is an effective strategy to enhance MOF stability, as the native Fe^{3+} structure collapses after only a single cycle.

Beyond the fundamental feat of achieving high porosity and high hydrolytic stability in the same MOF, materials able to reversibly adsorb water vapor are highly desired for energy saving applications such as in adsorption heat pumps as well as for humidification/dehumidification.[9] Highlighting the need for improvements in efficiency, climate control processes consume a vast share of our total primary energy, representing nearly 44% of US consumption.[10] Adsorption heat pumps may mitigate primary energy usage for heating and cooling by instead using waste heat resources to drive heating or cooling cycles. Further, dehumidification processes can substantially decrease the energy consumption of air conditioning and refrigeration by reducing the load coming from the heat of condensation of humid air. The water adsorption isotherm of Cr-*soc*-MOF-1 (Figure 2) indicates a stepwise uptake with onset at approximately

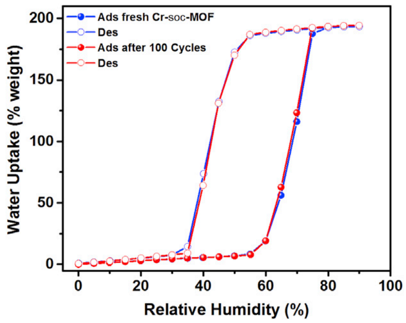

Figure 2. Water Uptake and Cycling of Cr-*soc*-MOF-1

Water adsorption isotherms for freshly prepared Cr-*soc*-MOF-1 (red) and after 100 cycles of water uptake (blue), demonstrating that the record water capacity of 200 wt% does not degrade with cycling. Image reproduced from Towsif Abtab et al.[3]

60% RH. Further, the framework will desorb water at approximately 40% RH. The difference in the adsorption and the desorption steps means that the framework could be ideal for applications in humidity control. Because optimal indoor humidity levels are approximately between 40% and 60% RH, the MOF will adsorb water vapor when the humidity is too high and release water vapor when room humidity falls too low. Although applications in adsorption heat pumps require less hysteresis between the adsorption and desorption curves to maximize efficiency, strategies to control the RH where these steps occur in MOFs are known[11] and can presumably be implemented in Cr-*soc*-MOF-1 as well.

The work of Towsif Abtab and coworkers represents an important advance in reticular chemistry methods and has produced a stable, exceptionally porous framework with record water uptake. For an immediate impact, the Cr-*soc*-MOF-1 is well suited for deployment in indoor humidity control. Moving forward, the elegant and mild synthesis of the Cr^{3+} framework reported here will serve as a guide for continued exploration of MOFs formed from inert metals, especially as more controlled syntheses, as enabled for instance by cation exchange, become more prominent. Future research incorporating inert metals into other framework topologies may provide important advances for many applications requiring both highly porous and highly stable materials.

1. Hendon, C.H., Rieth, A.J., Korzyński, M.D., and Dincă, M. (2017). Grand challenges and future opportunities for metal-organic frameworks. ACS Cent. Sci. *3*, 554–563.
2. Farha, O.K., Eryazici, I., Jeong, N.C., Hauser, B.G., Wilmer, C.E., Sarjeant, A.A., Snurr, R.Q., Nguyen, S.T., Yazaydın, A.Ö., and Hupp, J.T. (2012). Metal-organic framework materials with ultrahigh surface areas: is the sky the limit? J. Am. Chem. Soc. *134*, 15016–15021.
3. Towsif Abtab, S.M., Alezi, D., Bhatt, P.M., Shkurenko, A., Belmabkhout, Y., Aggarwal, H., Weseliński, Ł.J., Alsadun, N., Samin, U., Hedhili, M.N., and Eddaoudi, M. (2018). Reticular Chemistry in action: A hydrolytically stable MOF capturing twice its weight in adsorbed water. Chem *4*, 94–105.
4. Alezi, D., Belmabkhout, Y., Suyetin, M., Bhatt, P.M., Weseliński, L.J., Solovyeva, V., Adil, K., Spanopoulos, I., Trikalitis, P.N., Emwas, A.H., and Eddaoudi, M. (2015). MOF Crystal Chemistry paving the way to gas storage needs: Aluminum-based soc-MOF for CH_4, O_2, and CO_2 storage. J. Am. Chem. Soc. *137*, 13308–13318.
5. Férey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surblé, S., and Margiolaki, I. (2005). A chromium terephthalate-based solid with unusually large pore volumes and surface area. Science *309*, 2040–2042.
6. Akiyama, G., Matsuda, R., Sato, H., Hori, A., Takata, M., and Kitagawa, S. (2012). Effect of functional groups in MIL-101 on water sorption behavior. Microporous Mesoporous Mater. *157*, 89–93.
7. Jiao, Y., Morelock, C.R., Burtch, N.C., Mounfield, W.P., Hungerford, J.T., and Walton, K.S. (2015). Tuning the kinetic water stability and adsorption interactions of Mg-MOF-74 by partial substitution with Co or Ni. Ind. Eng. Chem. Res. *54*, 12408–12414.
8. Brozek, C.K., and Dincă, M. (2014). Cation exchange at the secondary building units of metal-organic frameworks. Chem. Soc. Rev. *43*, 5456–5467.
9. Rieth, A.J., Yang, S., Wang, E.N., and Dincă, M. (2017). Record atmospheric fresh water capture and heat transfer with a material operating at the water uptake reversibility limit. ACS Cent. Sci. *3*, 668–672.
10. US Energy Information Agency. (2015). Annual energy outlook 2015 with projections to 2040. https://www.eia.gov/outlooks/archive/aeo15/.
11. Wade, C.R., Corrales-Sanchez, T., Narayan, T., and Dincă, M. (2013). Post-synthetic tuning of hydrophilicity in pyrazolate MOFs to modulate water adsorption properties. Energy Environ. Sci. *6*, 2172–2177.