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MOF-5: Enthalpy of Formation and Energy Landscape of Porous Materials

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Supporting Information

ABSTRACT: The first experimental thermodynamic analysis of a metal−organic framework (MOF) has been performed. Measurement of the enthalpy of formation of MOF-5 from the dense components zinc oxide (ZnO), 1,4-benzenedicarboxylic acid (H_2BDC), and occluded *N*,*N*-diethylformamide (DEF) (if any) gave values of 78.64 ± 2.95 and 99.47 ± 3.62 kJ·[mol of $Zn_4O(BDC)_3 \cdot x$DEF$]^{-1}$ for the as-made form and the desolvated structure, respectively. These as-made and desolvated enthalpies correspond to the values 19.66 ± 0.74 and 24.87 ± 0.94 kJ·(mol of Zn$)^{-1}$, respectively. The energetics of desolvated MOF-5 per mole of Zn falls in line with trends relating the enthalpy of inorganic porous materials (zeolites, zeotypes, and mesoporous materials) to molar volume. MOF-5 extends a plateauing trend first suggested by thermodynamic studies of mesoporous materials. This leveling off of the destabilization energetics as the void space swells suggests that additional void volume beyond a certain point may begin to act as a parameter "external" to the structure and not destabilize it further. This could help explain the rich landscape of large-volume MOFs and their ease of desolvation.

Experimental thermochemical studies have touched many classes of porous materials: silica and aluminosilicate zeolites; germanosilicate, aluminophosphate, and gallophosphate zeotypes; and mesoporous silicas.[1] These studies have uncovered a complex energy landscape with many different structures having similar energies (Figure 1). Crystalline microporous materials with densities less than half those of their dense analogues (e.g., silica zeolites compared to quartz) are destabilized by only 7−15 kJ·(mol of tetrahedral units*$)^{-1}$ (* Tetrahedral units (TO_2)), making them accessible by chemical synthesis using structure-directing agents (SDAs) that interact only weakly with the framework. This thermochemical information has helped explain why some materials have resilient thermal and chemical stabilities while others do not.[2] It has also helped shed light on the mechanisms and driving forces for zeolite synthesis.[3]

Over the past decade, a new class of porous materials has emerged: metal−organic frameworks (MOFs). Interest in MOFs has surged as an impressive set of extremely low density materials with potential applications for gas storage, catalysis, gas sieving, luminescence, magnetism, and sensing have been discovered.[4]

Many MOFs endure to surprisingly high temperatures. For example, MOF-5, the subject of the present study, persists to 400 °C, which is within the typical range for most MOFs,[6] and there have been reports of MOFs that are stable to 500 °C,[7] suggesting high kinetic and/or thermodynamic stability. To date, no thermochemical analysis of any kind other than gas adsorption[8] has been performed on a MOF material.

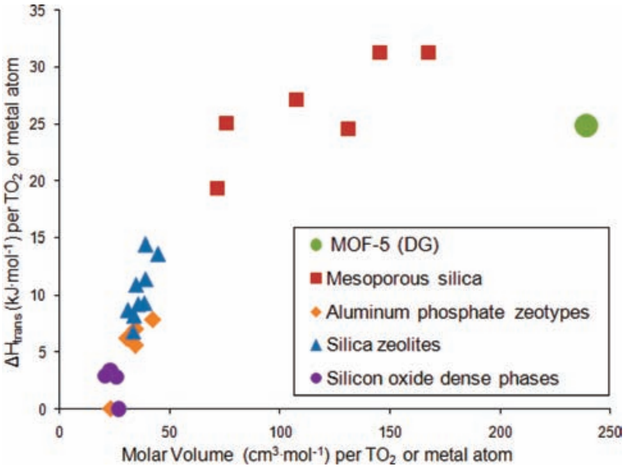

Figure 1. Enthalpy with respect to dense assemblages of porous materials as a function of molar volume.[5]

In MOFs, metal clusters dubbed secondary build units (SBUs) are bound together by multidentate organic molecules termed "organic linkers". Once a prototypical structure has been developed, controlled modifications of the organic linkers or changes in the composition of the SBUs can modify the structure and produce a large family of related frameworks, as demonstrated by isoreticular series of MOF materials.[9] The term "reticular chemistry" refers to the construction of MOFs by treating components as building blocks or "nets", allowing for a high level of synthetic control.[10] The rich series of structures formed suggests a complex energy landscape of accessible materials, analogous to that seen in purely inorganic frameworks.

MOFs extend the accessible porosity by at least an order of magnitude in comparison with zeolites and mesoporous materials.[4a] In this study, the molar volume of MOF-5 was found to be 238.94 cm^3·(mol of Zn$)^{-1}$, which is nearly an order of magnitude larger than that of MFI (ZSM-5), which has a molar volume of 33.51 cm^3·(mol of $SiO_2$$)^{-1}$.[11] The pore volume of MOF-5 is 1.4 times larger than that of the largest mesoporous material shown in Figure 1, SBA-15_26, which has a molar volume of 167.12 cm^3·(mol of $SiO_2$$)^{-1}$.[12]

Though there have been many novel developments in MOF synthetic design over the past decade,[13] MOF synthesis

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Table 1. Thermodynamic Cycle Used To Measure the Enthalpy of Formation of MOF-5 with Respect to Its Dense Components [ZnO, H_2BDC, and DEF (If Any)] via 5 M NaOH Room-Temperature Solution Calorimetry

reaction scheme	enthalpy measurement[a]
$4Zn^{2+}(aq) + 3BDC^{2-}(aq) + xDEF(aq) + 2OH^-(aq) \rightarrow Zn_4O(BDC)_3\cdot xDEF(cr) + H_2O(l)$	$\Delta H_1 = -\Delta H_s(\text{MOF-5})$
$4 \times [ZnO(cr) + H_2O(aq) \rightarrow Zn^{2+}(aq) + 2OH^-(aq)]$	$\Delta H_2 = 4\Delta H_s(ZnO)$
$3 \times [H_2BDC(cr) + 2OH^-(aq) \rightarrow BDC^{2-}(aq) + 2H_2O(aq)]$	$\Delta H_3 = 3\Delta H_s(H_2BDC)$
$x \times [DEF(l) \rightarrow DEF(aq)]$	$\Delta H_4 = x\Delta H_s(DEF)^b$
$3 \times [H_2O(aq) \rightarrow H_2O(l)]$	$\Delta H_5 = 3\Delta H_{dil}(H_2O)$
$4ZnO(cr) + 3H_2BDC(cr) + xDEF(l) \rightarrow Zn_4O(BDC)_3x(DEF)(cr) + 3H_2O(l)$	$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

[a] All of the ΔH_s values can be found in Table 3. [b] x values for MOF-5 (DEF) and MOF-5 (DG) can be found in Table 2.

Table 2. Physical Properties of MOF-5 (DEF) and MOF-5 (DG)

compound	solvent molecules (elemental analysis)	solvent molecules (TGA)	BET surface area ($m^2\cdot g^{-1}$)	pore volume ($cm^3\cdot g^{-1}$)	pore volume [$cm^3\cdot(\text{mol of Zn})^{-1}$]	ΔH_f [$kJ\cdot(\text{mol of Zn})^{-1}$]
MOF-5 (DEF)	7.4 ± 0.2	8 ± 1	290.4 ± 33.8			19.66 ± 0.74
MOF-5 (DG)	<0.2[a]	0 ± 0	2509.9 ± 43.3	1.24	238.7	24.87 ± 0.91

[a] The detection limit of the instrument was 0.2.

still remains largely empirical. While MOF synthesis emulates syntheses of zeolites and other porous materials in many ways,[5] the driving forces for MOF formation remain unclear. The removal of solvent from the pores after synthesis, analogous to the removal of water from a zeolite to "activate" it, is also a trial-and-error procedure. Underlying thermodynamic questions of stability versus metastability remain unanswered because of a complete lack of thermochemical data for any MOF. Are MOFs metastable with respect to their dense analogues, as are porous inorganic materials? Are MOFs strongly stabilized by inclusion of solvent, or, in analogy to SDA interactions in zeolites, does the solvent play a minor role in the energetics?

In this work, these questions have been addressed by measuring the enthalpies of formation of MOF-5 "as-synthesized" in *N*,*N*-diethylformamide (DEF) [herein called MOF-5 (DEF)] and desolvated MOF-5 [MOF-5 (DG)]. MOF-5 was chosen for thermodynamic analysis because of its simplicity, wide recognition, and prototypical nature. MOF-5 (DEF) was synthesized following the air-free procedure presented by Kaye.[14] MOF-5 (DG) was prepared by solvent exchange of MOF-5 (DEF) followed by heating under vacuum overnight, as prescribed by Kaye's method. Comparison of the powder X-ray diffraction patterns of MOF-5 (DEF) and MOF-5 (DG) with simulated diffraction patterns confirmed that both materials were single-phase MOF-5. The amount of DEF solvent in MOF-5 (DEF) and the absence of DEF in MOF-5 (DG) were confirmed by thermogravimetric analysis (TGA) combined with C,H,N elemental analysis. It was determined that there were 7.4 DEF molecules per formula unit in MOF-5 (DEF) and no detectable DEF in MOF-5 (DG) (Table 2).

Although the thermochemistries of zeolites and mesoporous materials have been studied by solution calorimetry in a molten oxide solvent at high temperature[2a] and hydrofluoric acid near room temperature,[15] respectively, a new methodology had to be developed for MOFs because of their totally different chemical compositions.[16] The enthalpy of formation of MOF-5 [$Zn_4O(BDC)_3\cdot xDEF$] from the dense components zinc oxide (ZnO), 1,4-benzenedicarboxylic acid (H_2BDC), and occluded DEF solvent (if any) was measured by solution calorimetry in aqueous sodium hydroxide solution (5 M NaOH) at room temperature. The overall formation reaction is given as reaction 1:

$$4ZnO + 3H_2BDC + xDEF \rightarrow Zn_4O(BDC)_3\cdot xDEF + 3H_2O \qquad (1)$$

The measured values of the solution enthalpy (ΔH_s) (Table 3) were applied to the thermodynamic cycle shown in Table 1 to determine the heat of formation (ΔH_f) of MOF-5 (i.e., ΔH_{rxn} for reaction 1). The obtained values of ΔH_f are 78.64 ± 2.95 and 99.47 ± 3.62 kJ·(mol of MOF-5)$^{-1}$ for MOF-5 (DEF) and MOF-5 (DG), respectively. These are equivalent to 19.66 ± 0.74 and 24.87 ± 0.91 kJ·(mol of Zn)$^{-1}$ for MOF-5(DEF) and MOF-5 (DG), respectively (see Tables 2 and 3). This means that both solvated and desolvated MOF-5 are energetically metastable with respect to the dense-phase assemblages. The enthalpy per mole of tetrahedral cation relative to dense phases of desolvated MOF-5 (DG) follows the energetic trend observed for inorganic porous materials (see Figure 1).

The Zn−O bond lengths in the reported single-crystal structure of MOF-5,[17] the single-crystal structure of basic zinc acetate[18] (which emulates the SBU in MOF-5), and hexagonal ZnO[19] are all very similar (Table S2 in the Supporting Information). The bond angles in all three are also in agreement (Table S2). These similarities suggest that the energetic differences between the dense assemblages and the final MOF stem from the void space in MOF-5. ZnO has a framework density (FD) of 42.0 Zn·nm^{-3}, whereas that for MOF-5 is 1.9 Zn·nm^{-3}. This large difference clearly illustrates the immense porosity of MOF-5. Despite its very low FD, its enthalpy falls on the trend of energetics versus molar volume established by the inorganic materials. Clearly, MOF-5 is only moderately destabilized despite the extreme openness of its structure.

The solvent interactions in MOF-5 also mirror the energetics found in other porous materials. The enthalpies of DEF solvation have an average value of -5.2 ± 1.6 kJ·(mol of Zn)$^{-1}$. This falls in line with exothermic SDA interactions measured in zeolites, which range from -1.0 to -6.0 kJ·(mol of SiO_2)$^{-1}$.[20] Thus, the DEF present in the "as-synthesized" MOF-5 stabilizes the

Table 3. Calorimetric Data Applied to the Thermodynamic Cycle To Determine the Enthalpies of Formation of MOF-5 (DEF) and MOF-5 (DG)

compound	ΔH_s (kJ·mol^{-1})	ΔH_f [kJ·(mol of $Zn_4O(BDC)_3 \cdot x$DEF)$^{-1}$]	ΔH_f [kJ·(mol of Zn)$^{-1}$]	$\Delta H^\circ_{f,el}$ (kJ·mol^{-1})
ZnO	-0.34 ± 0.28			-350.46 ± 0.27[a]
H_2BDC	-70.07 ± 0.12			-816.3 ± 1.5[b]
DEF	-4.30 ± 0.01			
H_2O	0.5[c]			-285.83 ± 0.04[a]
MOF-5 (DEF)	-320.53 ± 2.69	78.64 ± 2.95	19.66 ± 0.74	[d]
MOF-5 (DG)	-309.55 ± 5.09	99.47 ± 3.62	24.87 ± 0.91	-2893.78 ± 5.88

[a] Reference 21. [b] Reference 22. [c] Reference 23. [d] Not calculated because $\Delta H^\circ_{f,el}$ for DEF is not known.

MOF-5 framework only slightly, as is the case for zeolite—SDA interactions.

Thus, the occluded solvent may be space-filling rather than energetically important. The relative ease of solvent removal without collapse of the framework supports the finding of such weak interactions.

The small metastability of MOF-5 probably reflects its robust Zn—O bonds, which are very similar to the Zn—O bonds in ZnO. The relatively modest energetic destabilization of MOF-5 with respect to its dense assemblage is consistent with the observed good thermal stability of the porous framework in the absence of moisture. Despite the fact that its molar volume is 70 cm^3·mol^{-1} larger than that of the largest mesoporous silica material measured, its enthalpy relative to the dense phases falls within the spread of enthalpies for mesoporous silica. This suggests a plateau of the enthalpy relative to the dense phases as the molar volume increases. Such a plateau may imply that the large free volume in the pores does not influence the energetics of the part of the structure in which the bonded atoms are concentrated. Indeed, one may perhaps begin to think of the void space as a second phase. The larger voids then would not strongly affect the energetics. This may be the key to the easy accessibility of even more porous structures, such as the largest reported MOF, MOF-210, which has a pore volume of 1636.21 cm^3·(mol of Zn)$^{-1}$,[4a] nearly 7 times larger than that of MOF-5 (DG). The data in Figure 1 show a trend with some scatter rather than a smooth curve. The scatter may reflect specific structural factors (symmetry, wall thickness, amorphous vs crystalline structure). Nevertheless, a general trend with decreasing slope is seen, and MOF-5 follows the pattern established by the energetic investigations of zeolites and mesoporous materials. Calorimetric studies of MOFs of lower density will provide more definitive evidence for or against a plateau in energetics. This measurement for MOF-5 is the first determination of the enthalpy of formation for any MOF, and calorimetric studies of other MOFs are in progress.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental information, sample characterization data, and solution calorimetry procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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