



Thermodynamics of metal-organic frameworks



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ABSTRACT

Although there have been extensive studies over the past decade in the synthesis and application of metal-organic frameworks (MOFs), investigation of their thermodynamic stability and of the energetics of guest–host interactions has been much more limited. This review summarizes recent progress in experimental (calorimetric) determination of the thermodynamics of MOF materials. The enthalpies of MOFs relative to dense phase assemblages suggest only modest metastability, with a general increase of enthalpy with increasing molar volume, which becomes less pronounced at higher porosity. The energy landscape of nanoporous materials (inorganic and hybrid) consists of a pair of parallel patterns within a fairly narrow range of metastability of 5–30 kJ per mole of tetrahedra in zeolites and mesoporous silicas or per mole of metal in MOFs. Thus strong thermodynamic instability does not seem to limit framework formation. There are strong interactions within the chemisorption range for small molecule–MOF interactions with defined chemical binding at the metal centers or other specific locations. Coexistence of surface binding and confinement can lead to much stronger guest–host interactions.

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1. Introduction

Developments in synthetic chemistry and materials science enable fabrication of metal-organic frameworks (MOFs) with extremely high surface areas, huge accessible porosity and tunable chemical properties [1–3]. Due to these unique properties, MOFs are considered to have a promising future for application in energy storage [4–9], catalysis [10–13], adsorption/separation [14,15], molecular sensing [16–18] and medicine [19–21]. So far more than six thousand distinct structures have been developed [1] (see Fig. 1 for some examples of structures). These structures consist of metal centers connected by organic linkers. The length and chemical complexity of the linker defines the porosity and both the metal and linker define the physical and chemical properties [22]. Although some MOFs have been commercialized (such as HKUST-1, which is produced by BASF and labeled as Basolite[®] C 300), others, despite favorable properties, cannot be applied due to stability related issues such as poor thermal/hydrothermal sustainability, phase transition/decomposition under operating conditions and/or framework collapse after removing solvent from their as-made forms. Also, the underlying rules governing MOF formation and modification are still vague and largely empirical. These topics, as well as several unanswered questions, including the potential porosity limit and magnitude of guest–host interactions, are of particular interest and are

fundamentally governed by thermodynamics. Calorimetry offers a direct approach to determining such thermodynamic parameters.

The thermodynamic investigation of nanoporous frameworks initially focused on thermochemical studies of inorganic microporous and mesoporous materials, in which various calorimetric methodologies (differential scanning calorimetry (DSC), high temperature oxide melt solution calorimetry and hydrofluoric acid solution calorimetry) have been employed to investigate the energetics of different phases, with an emphasis on pure silica polymorphs [23–41]. In these studies on inorganic frameworks (zeolites, mesoporous silicas, aluminum phosphates) [23–41], three key topics have been explored and discussed in detail (1) the formation (transition) enthalpy of porous materials relative to their dense phase oxides [24,27,28,30,33,35,36,39], (2) structure-directing agent (SDA)–framework interactions [38,42], and (3) in-situ studies on zeolite synthesis mechanisms [31,32,34]. A major conclusion is that inorganic porous materials are only modestly metastable with respect to their respective dense phase oxides. The degree of this metastability tends to increase as the molar volume of that material (per TO₂ unit) increases (see the blue plot in Fig. 1). However, the destabilization seems to approach a plateau, or at least increase only slightly, at high porosity. Furthermore, the interaction between the frameworks and their structure-directing organic molecules are relatively weak.

Such thermodynamic studies are being extended to MOFs, which have even more open structures. These studies not only provide valuable insights on the origin of MOF properties, but also reveal underlying principles for synthesis of new structures, and further enrich the overall energetic landscape of porous materials.

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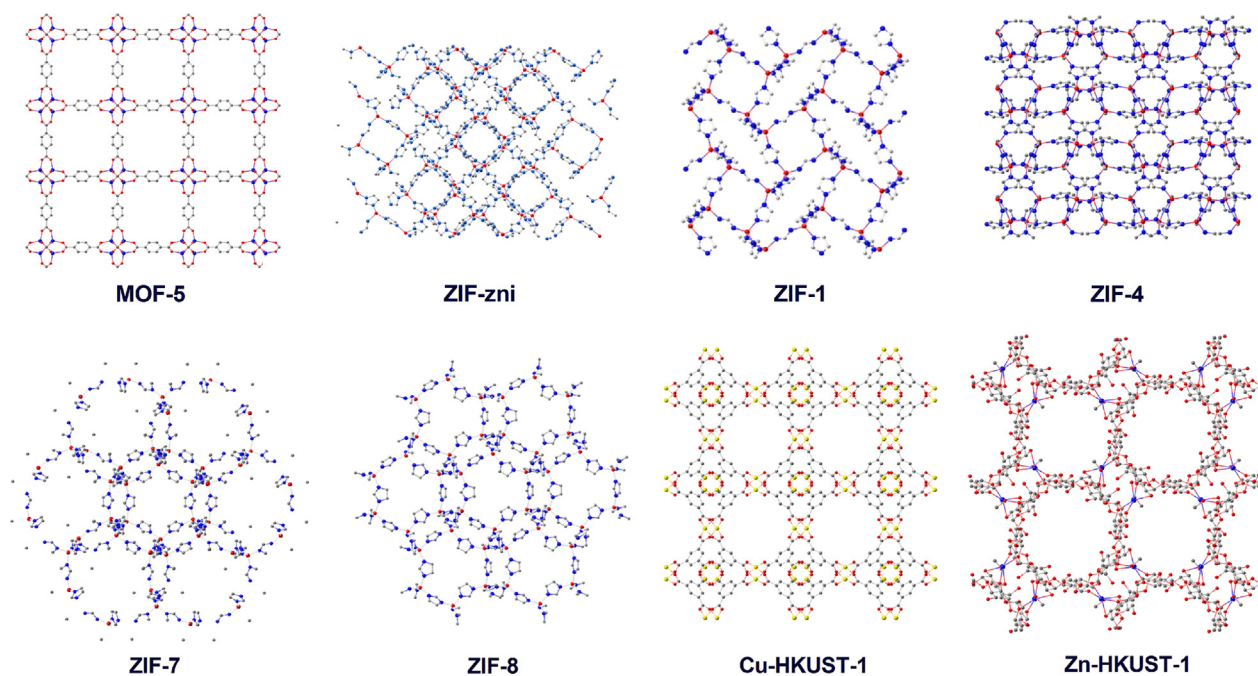


Fig. 1. Crystallographic structures of metal-organic frameworks discussed in this review. C atoms are shown in gray, O atoms in red, Zn atoms in blue, and Cu atoms in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

High temperature oxide melt solution calorimetry utilized for inorganic materials is generally not applicable to such hybrid materials because of the large exothermic effects associated with the oxidation (burning) of the organic linkers. Instead, solution calorimetry at room temperature using various solvents (NaOH, HCl and HCl/DMF binary mixtures), tailored to dissolving both the organic and inorganic constituents for a specific MOF, has been developed. Frameworks investigated include several representative structures, MOF-5, a group of ZIFs, Cu and Zn HKUST-1, and CD-MOF-2. In addition, interactions from confinement/adsorption of various guest molecules in MOFs have been quantitatively determined. This review summarizes recent progress in the UC Davis Peter A. Rock Thermochemistry Laboratory on the energetics of MOFs. Unless otherwise noted, all results presented are experimentally determined.

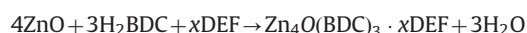
2. Energetics of metal-organic frameworks

2.1. MOF-5

As one of the first synthesized MOF structures, MOF-5 is a canonically constructed cubic 3-D network formed by connecting $(\text{Zn}_4\text{O})^{6+}$ tetrahedra and 1,4 benzenedicarboxylate (bdc^{2-}) linkers [43]. Upon removal of solvent (diethyl formamide (DEF)), it has huge surface area up to $2500 \text{ m}^2/\text{g}$ and accessible porosity as much as 240 cm^3 per mole of Zn, which is even larger than that of the most open mesoporous silicas (around 200 cm^3 per mole of SiO_2) [43]. MOF-5 can be thermally stable up to $500 \text{ }^\circ\text{C}$ in the absence of moisture [44]. These unique properties have raised a series of questions concerning the thermodynamics of MOFs. As crystalline solids metastable relative to their dense assemblages, how large is this energy difference and does the inclusion of organics stabilize the extremely open frameworks; or do the solvent molecules just act as space-fillers?

The first thermochemical investigation of a MOF [45] determined the enthalpy of formation of as-made and activated MOF-5 from zinc oxide (ZnO), 1,4-benzenedicarboxylic acid (H_2bdc), and

confined solvent *N,N*-diethylformamide (DEF) by solution calorimetry in aqueous NaOH. The overall formation reaction of MOF-5 is represented by



The enthalpies of formation obtained are 19.7 ± 0.7 and $24.9 \pm 0.9 \text{ kJ/mol Zn}$ for as-made and activated MOF-5, respectively. These results show that both forms are energetically less stable than their dense phase assemblage, with metastability comparable to that found in silica systems (see Fig. 2). Thus, the results suggest that MOF-5 is only moderately destabilized despite its extremely open structure. This observation may imply that further increasing of free, internal void space may not strongly affect the framework energetics.

For zeolites, the SDA–framework interactions have been determined to be -1.0 to $-6.0 \text{ kJ/mol SiO}_2$ [37]. Confinement of DEF in as-made MOF-5 returned an enthalpy of interaction of $-5.2 \pm 1.6 \text{ kJ/mol Zn}$. Thus, the small magnitude of this interaction is a strong indication that the DMF molecules act mainly as passive “space fillers”, instead of chemically supporting the structure strongly in a thermodynamic sense.

2.2. Zeolite imidazolate frameworks (ZIFs)

Zeolite imidazolate frameworks (ZIFs) possess hybrid chemical natures as well as zeolitic structural units ($\text{M}(\text{Imidazolate})_4$ analogous to SiO_4 in siliceous zeolites) [46,47]. They feature extremely open frameworks, large surface areas and versatile chemical and structural properties [46,47]. Some ZIFs preserve impressive mechanical and thermal stability up to $500 \text{ }^\circ\text{C}$ [48]. Energetics of ZIFs have been studied by computational methods such as density functional theory (DFT), which predict that ZIFs tend to be less stable or with higher energy as the porosity increases, or framework density (FD) decreases [49]. Hughes et al. performed calorimetric measurements on several ZIFs (ZIF-zni, ZIF-1, ZIF-4, ZIF-7 and ZIF-8) using room temperature aqueous solution calorimetry (5 M NaOH) [50]. The enthalpies of formation of the activated/dessolvated ZIFs were measured and analyzed with respect to

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