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# 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.

## 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 $TO_2$ 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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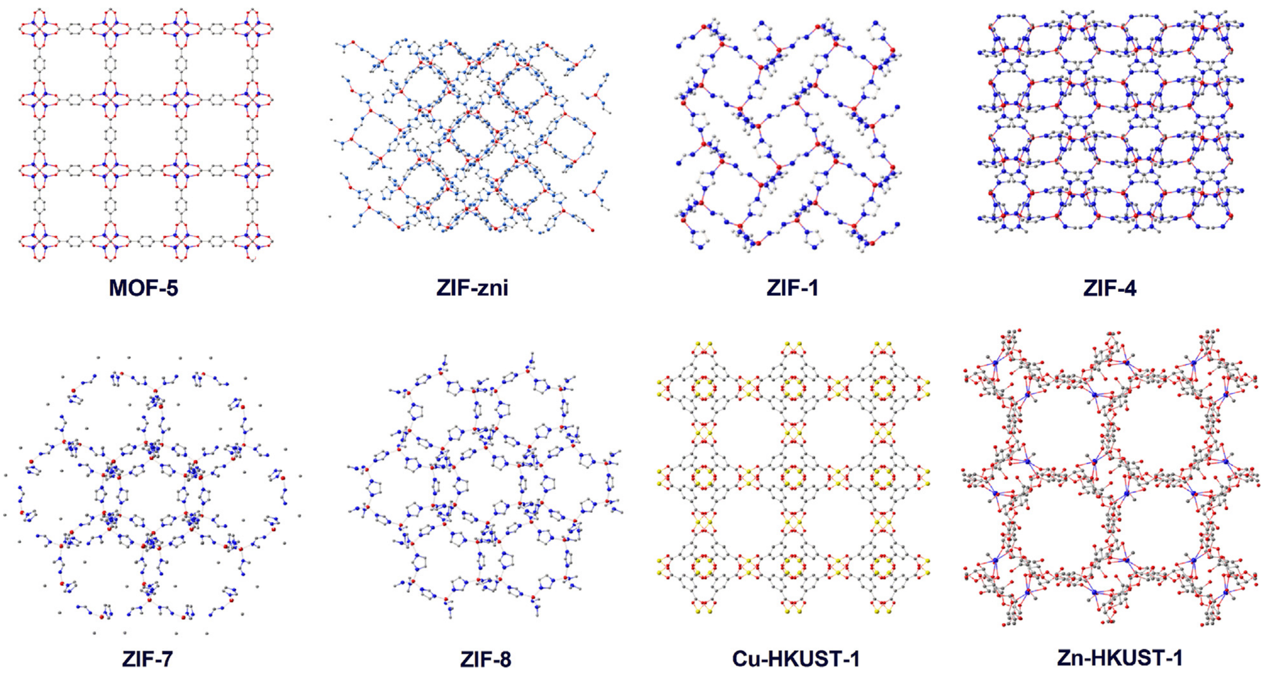

**Fig. 1.** Crystallographic structures of metal-organic frameworks discussed in this review. C atoms are shown in gray, O atoms in red, Zn atoms in blue, and Cu atoms in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 $(Zn_4O)^{6+}$ tetrahedra and 1,4 benzenedicarboxylate ($bdc^{2-}$) linkers [43]. Upon removal of solvent (diethyl formamide (DEF)), it has huge surface area up to 2500 $m^2/g$ 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 °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

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

The enthalpies of formation obtained are $19.7 \pm 0.7$ and $24.9 \pm 0.9$ 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 $-6.0$ kJ/mol $SiO_2$ [37]. Confinement of DEF in as-made MOF-5 returned an enthalpy of interaction of $-5.2 \pm 1.6$ 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 ($M(Imidazolate)_4$ 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 °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 their dense phase counterparts, metal oxides (ZnO or CoO) and imidazolate linkers (see Table 1 and Fig. 2). Experimental observations suggest that the enthalpies of solution of all ZIFs at 25 °C are exothermic. Moreover, although the porosity of ZIFs increases by nearly a factor of two, from 135.9 to 248.8 $cm^3$/mol, the energetics only covers a fairly narrow range of 13.0–27.2 kJ/mol Zn. Again, this thermochemical evidence indicates that ZIFs only have modest metastability and this destabilization tends to increase more slowly as the framework density decreases.

Table 1 lists the calorimetric results and structural parameters for various MOFs. The combination of enthalpy of formation data for MOF-5 and ZIFs defines a trend for hybrid porous materials (see Fig. 2). These enthalpies form a parallel pattern mirroring the observed trend for inorganic porous structures but slightly displaced from it. Both curves have decreasing slopes as framework molar volume increases. The displacement of these two curves presumably originates from variation in their chemical natures such as building units (hybrid versus inorganic), bonds (ionic versus covalent), surface properties and the different reference states for dense phases. There is no physical reason for a single master curve but, nevertheless, the very similar behavior of inorganic phases and hybrid materials is striking. The observed energy landscape indicates that for ultraporous materials, inorganic or hybrid, further increase of void space may not compromise framework stability. Instead, ultra-high porosity is very likely to be enabled by rational design of stronger bonds between metal atoms and organic linkers or engineering of building units with better mechanical properties. In other words, there is no immediate thermodynamic barrier preventing further development of ultraporous materials.

Solvent–framework interactions were also investigated on as-made ZIF-4 with per mole DMF. A weak interaction, similar as that in MOF-5 with DEF, was found ( $-2.8 \pm 0.9$ kJ/mol Zn).

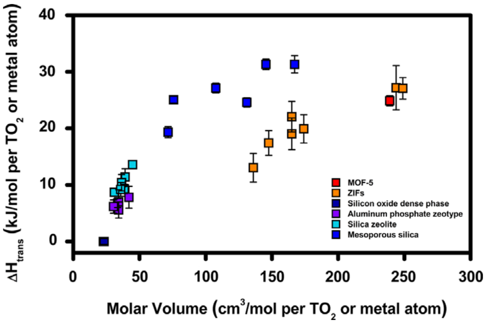

**Fig. 2.** Energy landscape of inorganic and hybrid porous materials.

### 2.3. *Paddle wheel metal-organic frameworks (Cu and Zn HKUST-1)*

For MOFs without defined built-in binding sites, such as MOF-5 and ZIFs, solvent molecules only passively fill the pores with weak framework interactions. Upon removal of solvent, the crystalline nanoporous structures persist. Yet another, entirely distinct phenomenon has been observed for paddle wheel MOFs, such as HKUST-1, which contain "open" metal binding sites capable of strongly coordinating additional molecules [51,52]. Using room temperature acid solution calorimetry in a binary solvent (HCl/DMF), Bhunia et al. examined both the as-synthesized and activated Cu and Zn polymorphs of HKUST-1 [53]. The formation enthalpies with respect to their dense assemblages (ZnO or CuO, trimesic acid (TMA), and N,N-dimethylformamide (DMF)) were derived from the measured heats of solution. The enthalpies of formation of as-made Cu-HKUST-$H_2O$ (($Cu_3TMA_2 \cdot 3H_2O$) · 5DMF) and Zn-HKUST-DMF (($Zn_3TMA_2 \cdot 3DMF$) · 2DMF) are $-52.7 \pm 0.3$ kJ/mol Cu and $-54.2 \pm 0.6$ kJ/mol Zn, respectively. These negative enthalpies result from strong solvent stabilization rather than from intrinsic framework stability. For activated Cu-HKUST-dg ($Cu_3TMA_2$), ("dg" denotes "degassed") and Zn-HKUST-amorphous ($Zn_3TMA_2 \cdot 2DMF$), formation enthalpies are $16.7 \pm 0.5$ kJ/mol Cu and $-3.6 \pm 0.2$ kJ/mol Zn, respectively. The enthalpy of solvent–framework interaction is measured as $-69.4$ kJ/mol Cu for Cu-HKUST-$H_2O$ and that for the HKUST-1–DMF interaction is estimated to be equal to or more negative than $-50.7$ kJ/mol Zn. These large exothermic enthalpies provide strong evidence that DMF molecules are bonded strongly onto the open metal sites within the HKUST-1 structure. Indeed the copper polymorph partially amorphizes on attempted solvent removal. The solvent–framework interaction in the HKUST-1 structure is strong enough to be considered chemisorption. This interaction has similar strength as that of bonding of $H_2O$ on transition metal oxide nanoparticle surfaces and zeolites, which indicates the solvent molecule may play a very active role in stabilizing the secondary building unit (SBU) as well as relaxing the energy of the whole porous structure.

## 3. Guest–host interactions within metal-organic framework

### 3.1. *Iodine confinement in ZIF-8*

ZIF-8 (Zn(2-methylimidazolate)$_2$) is a promising material for the capture of radioactive iodine originating from nuclear sources [54–56]. The interactions between iodine and ZIF-8 [46] have been investigated using aqueous solution calorimetry, using a biphasic solvent of of 5 M HCl and $CHCl_3$ at room temperature [57]. Two

**Table 1**
Basic structural properties and energetics of metal-organic frameworks investigated by calorimetry.

| Framework | Formula | BET area ($m^2$/g) | Molar volume ($cm^3$/mol metal) | $\Delta H_s$ (kJ/mol formula) | $\Delta H_f$ (kJ/mol metal) | $\Delta H_{trans}$ (kJ/mol metal) | $\Delta H^\circ_{f,298\ K}$ (kJ/mol formula) |
|---|---|---|---|---|---|---|---|
| MOF-5 · DEF | $Zn_4O(bdc)_3 \cdot 7.4DEF$ | 290.4 | *N/A* | $-320.5 \pm 2.7$ | $78.6 \pm 3.0$ | $19.7 \pm 0.7$ | |
| MOF-5 | $Zn_4O(bdc)_3$ | 2509.9 | 238.7 | $-309.6 \pm 5.1$ | $99.5 \pm 3.6$ | $24.9 \pm 0.9$ | $-2893.78 \pm 0.9$ |
| ZIF-zni | $Zn(Im)_2$ | 4 | 135.9 | $-109.6 \pm 0.9$ | $-33.6 \pm 1.6$ | $13.0 \pm 2.5$ | $1.3 \pm 3.1$ |
| $_{am}$ZIF-4 | $Zn(Im)_2$ | 10 | 147.6 | $-114 \pm 0.5$ | $-29.2 \pm 1.2$ | $17.4 \pm 2.2$ | $5.7 \pm 2.7$ |
| ZIF-4 · DMF | $Zn(Im)_2 \cdot 1.8DMF$ | | *N/A* | $-135.7 \pm 0.8$ | $-27.6 \pm 1.9$ | $19.0 \pm 2.8$ | $-423.6 \pm 7.8$ |
| ZIF-4 | $Zn(Im)_2$ | 300 | 165 | $-118.6 \pm 1.1$ | $-24.6 \pm 1.8$ | $22.1 \pm 2.7$ | $10.3 \pm 3.2$ |
| CoZIF-4 | $Co(Im)_2$ | | 165 | $-158.4 \pm 0.8$ | $-18.4 \pm 1.7$ | $28.3 \pm 2.7$ | $129.2 \pm 4.2$ |
| ZIF-1 | $Zn(Im)_2$ | | 174.1 | $-116.5 \pm 0.8$ | $-26.7 \pm 1.6$ | $19.9 \pm 2.5$ | $8.2 \pm 3.0$ |
| ZIF-7 | $Zn(bIm)_2$ | | 243.8 | $-91.3 \pm 2.6$ | $-19.5 \pm 3.0$ | $27.2 \pm 3.9$ | $74.9 \pm 5.8$ |
| ZIF-8 | $Zn(mIm)_2$ | 1724 | 248.8 | $-138.4 \pm 0.6$ | $-19.6 \pm 1.0$ | $27.1 \pm 1.9$ | $-81.5 \pm 2.8$ |
| Cu-HK-1 · $H_2O$ | $(Cu_3TMA_2 \cdot 3H_2O) \cdot 5DMF$ | | | $23.5 \pm 1.1$ | $-52.7 \pm 0.3$ | | $-4203.5 \pm 15.0$ |
| Cu-HKUST-1 | $Cu_3TMA_2$ | 1776 | | $-137.3 \pm 1.5$ | $16.7 \pm 0.5$ | | $-1940.9 \pm 6.4$ |
| Zn-HK-1 · DMF | $(Zn_3TMA_2 \cdot 3DMF) \cdot 2DMF$ | | | $-22.0 \pm 1.5$ | $-54.2 \pm 0.6$ | | $-3933.8 \pm 10.2$ |
| Zn-HK-1 · amorph | $Zn_3TMA_2 \cdot 2DMF$ | | | $-128.3 \pm 0.4$ | $-3.6 \pm 0.2$ | | $-3063.6 \pm 5.5$ |

$\Delta H_s$, enthalpy of solution at 298 K; $\Delta H_f$, enthalpy of formation from metal oxide and organic components; $\Delta H_{trans}$, enthalpy of transition; $\Delta H^\circ_{f,298\ K}$, standard enthalpy of formation from elements; HK-1 denotes HKUST-1, Refs. [1–3].

iodine-containing ZIF-8 samples were tested. One was used as prepared; it included 0.17 $I_2$/Zn adsorbed on the external surfaces and 0.59 $I_2$/Zn confined within the cages. The other sample was treated at 125 °C, leaving only confined iodine (0.59 $I_2$/Zn). Calorimetric data suggest that the interaction enthalpies between iodine and ZIF-8 are $-18.1 \pm 0.6$ kJ/mol $I_2$ (relative to solid $I_2$) for surface-adsorbed iodine and $-41.5 \pm 2.0$ kJ/mol $I_2$ for cage-confined iodine. Confinement of iodine within ZIF-8 results in three times stronger bonding than for iodine adsorption on other organic or carbon adsorbents, which exhibit much less exothermic heat effects ($-5$ to $-15$ kJ/mol $I_2$). Once confined in the cage, which in ZIF-8 is of just the right size for the $I_2$ molecule to bridge to two imidazole groups, each iodine molecule is able to bond with two opposing 2-methylimidazolate linkers, forming two charge transfer (CT) complexes, exhibiting strong exothermic heat effects. In contrast, the iodine on the external surfaces of ZIF-8 can only be adsorbed onto one imidazole, resulting in much weaker overall binding. Hence, the combination of chemisorption with cage confinement results in exceptionally strong interactions, which may have promising future application in separation and waste treatment processes.

### *3.2. Adsorption calorimetry of carbon dioxide on carbohydrate metal-organic frameworks (CD-MOF-2)*

CD-MOF-2 is an environmentally benign compound made of sugar and alkali metal oxide and having a strong affinity for binding carbon dioxide [58] through interaction with the hydroxyl groups on the sugar molecules. Gas adsorption calorimetry, initially developed for the study of water binding on nanoparticle surfaces, provides simultaneous measurement of the adsorption isotherm and the heat of adsorption as a function of coverage [59]. The data obtained are independent of any model of adsorption and are particularly useful for framework materials showing strong and/or complex adsorption behavior, sometimes with several distinct steps relating to adsorption on different sites. The measured differential enthalpies, which are heat effects associated with adsorption per mole of adsorbate at a given coverage, show different plateaus as a function of gas loading, reflecting different stages of reaction as sorption evolves (see Fig. 3). Specifically for CD-MOF-2, at near-zero coverage, the strongest, irreversible binding results in an exothermic heat effect of $-113.5 \pm 0.9$ kJ/ mol $CO_2$ and involves only a small number of hydroxyl groups. The less strong, major chemisorption event is reversible and seen as a plateau in enthalpy, liberating a heat of $-65.4 \pm 1.6$ kJ/mol $CO_2$, and occurs on the less reactive major fraction of hydroxyl groups. Finally, a second plateau concludes the gas–MOF interaction with a physisorption of $-40.0 \pm 1.8$ kJ/mol $CO_2$ [60]. Thus, this study suggests the existence of at least two energetically distinct chemisorption binding sites for $CO_2$ on CD-MOF-2. In a broader sense, direct adsorption calorimetry is a powerful technique mapping MOF materials with various types of strong and/or defined chemisorption sites (e.g. functional groups and empty metal orbitals).

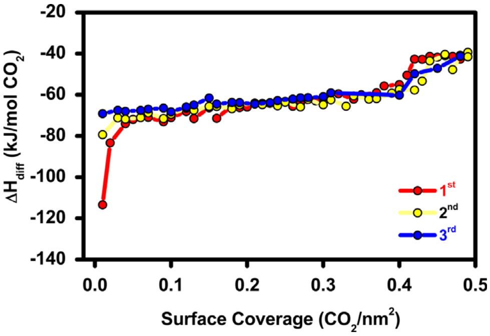

**Fig. 3.** Differential enthalpies of $CO_2$ adsorption at 25 °C for the first, second and third round of adsorption on the same CD-MOF-2 sample.

### *3.3. Adsorption calorimetry of xenon (Xe) and krypton (Kr) on copper HKUST-1*

Differential heats of adsorption on Cu HKUST-1 have been determined for for Xe and Kr [61]. The zero-coverage adsorption enthalpies (see Fig. 4) are $-26.0 \pm 1.0$ and $-18 \pm 1.0$ kJ/mol for Xe and Kr, respectively, suggesting weak, physical interactions. As more gas molecules are loaded, the heats of adsorption for both gases become less exothermic. Other investigations, X-ray and neutron scattering, and Grand Canonical Monte Carlo simulation suggest that there is no evidence for direct interaction between open copper sites and the noble gas molecules [61]. Hence, at near-zero coverage, the affinity between these noble gases may mainly arise from confinement of atoms inside the smallest pores of HKUST-1. This work indicates that for noble gas adsorption/separation, the confinement effect from microporosity may be the key factor governing material performance. Table 2 summarizes the enthalpies of interaction for various MOF based guest–host systems (also see Fig. 5).

## 4. Conclusions and outlook

Thermochemical studies on MOFs lead to several inferences and implications. Similar to that of inorganic porous materials, MOFs are only moderately metastable compared to their dense phase assemblages. It may be possible to introduce even greater porosity with little energetic penalty and to rationally design MOFs with ultra-high porosity and/or surface area. There are only

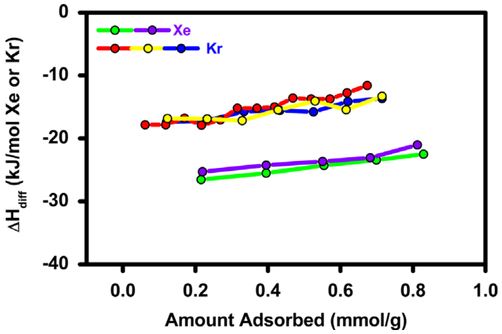

**Fig. 4.** Differential enthalpies of adsorption at 25 °C as a function of gas loading for Xe and Kr on HKUST-1.

**Table 2**
Enthalpies of interaction for confinement or adsorption of various guest molecules in metal-organic framework hosts.

| Guest molecule | Host metal-organic framework | Enthalpy of interaction (kJ per mole of guest molecules) |
|---|---|---|
| Chemisorbed $CO_2$ | CD-MOF-2 | $-65.4 \pm 1.6$ |
| $H_2O$ | Cu-HKUST-1 | $-65.0 \pm 6.0$ |
| Cage-confined $I_2$ | ZIF-8 | $-41.5 \pm 2.0$ |
| Xe | Cu-HKUST-1 | $-26.0 \pm 1.0$ |
| Surface-adsorbed $I_2$ | ZIF-8 | $-18.1 \pm 0.6$ |
| Kr | HKUST-1 | $-18.0 \pm 1.0$ |
| DEF | MOF-5 | $-2.8 \pm 0.9$ |
| DMF | ZIF-4 | $-1.7 \pm 0.4$ |

Refs. [61–67].

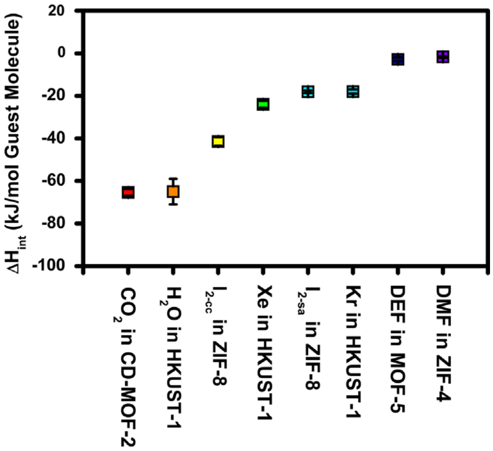

**Fig. 5.** Enthalpies of interaction at 25 °C for various confinement systems with MOFs as hosts. Color mapping from red to blue represents decreasing enthalpy. Subscripts "cc" and "sa" denote "cage-confined" and "surface-adsorbed", respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

weak interactions between confined solvents and MOF frameworks unless there is identifiable strong chemical bonding at specific sites. When such strong interactions exist, guest adsorption isotherms can be complex and there may be several distinguishable adsorption steps as a function of coverage. Gas adsorption calorimetry is an excellent tool for studying such complex adsorption phenomena.

Our planned future work includes enthalpy of formation/transition measurement of ultra-high porous (ultra-low density) MOFs up to 7000 ~ 10,000 $m^2/g$ to explore possible phase stability limits and obtain insights about synthesis pathways/mechanisms. Additional adsorption (gas) and immersion (liquid) calorimetric experiments can be performed to investigate the strength and mechanisms of guest–host interactions in MOFs with emphasis on the interplay between surface binding and confinement. In particular, guest molecules crucial to energy storage, catalysis, gas separation, environmental remediation and medicine can be studied.

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