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Thermochemistry of Zeolitic Imidazolate Frameworks of Varying Porosity

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Supporting Information

ABSTRACT: The first thermochemical analysis by room-temperature aqueous solution calorimetry of a series of zeolite imidazolate frameworks (ZIFs) has been completed. The enthalpies of formation of the evacuated ZIFs—ZIF-zni, ZIF-1, ZIF-4, CoZIF-4, ZIF-7, and ZIF-8—along with as-synthesized ZIF-4 (ZIF-4-DMF) and ball-milling amorphized ZIF-4 (*a*_mZIF-4) were measured with respect to dense components: metal oxide (ZnO or CoO), the corresponding imidazole linker, and *N,N*-dimethylformamide (DMF) in the case of ZIF-4-DMF. Enthalpies of formation of ZIFs from these components at 298 K are exothermic, but the ZIFs are metastable energetically with respect to hypothetical dense components in which zinc is bonded to nitrogen rather than oxygen. These enthalpic destabilizations increase with increasing porosity and span a narrow range from 13.0 to 27.1 kJ/mol, while the molar volumes extend from 135.9 to 248.8 cm³/mol; thus, almost doubling the molar volume results in only a modest energetic destabilization. The experimental results are supported by DFT calculations. The series of ZIFs studied tie in with previously studied MOF-5, creating a broader trend that mirrors a similar pattern by porous inorganic oxides, zeolites, zeotypes, and mesoporous silicas. These findings suggest that no immediate thermodynamic barrier precludes the further development of highly porous materials.

Zeolitic imidazolate frameworks (ZIFs), a family of low-density porous organic–inorganic hybrid materials, are of increasing interest. Spanning the intersection between metal–organic frameworks (MOFs) and zeolitic structures, ZIFs offer tunable and chemically versatile structures, while retaining zeolitic traits of thermal and chemical stability.^{1,2} Understanding their mechanical, chemical, and thermal stability is critical to applications. Elastic moduli, hardness, and shear moduli^{3–5} as well as response to thermal treatment⁶ have been reported. Computational studies reveal a trend of increasing energy with decreasing density.^{7–9}

Some crystalline ZIFs amorphize on heating,⁶ ball-milling,^{10,11} and application of hydrostatic pressure.¹² However, several ZIFs persist with little or no structural change to temperatures near 500 °C.¹³ Over 100 distinct ZIF frameworks currently exist, displaying a range of gas sorption, separation, catalytic, magnetic, and sensing abilities.^{14–17} The multitude of polymorphs arises from the striking similarity of basic building

blocks in ZIFs, M(Im)₄ (Im = imidazolate), to the SiO₄ unit in zeolites for which at least 40 unique polymorphs of siliceous zeolites are known.¹⁸ Experimental evaluation of the energetics of zeolites, aluminophosphate zeotypes, and related mesoporous silica materials has been undertaken by a variety of calorimetric methods, revealing that metastability is modest but increases with molar volume.^{19–24} For example, silica zeolites all have enthalpies within a surprisingly small range, 7–15 kJ per mole of SiO₂, with respect to quartz, despite having a wide range of molar volumes, 19.4–46.5 cm³/mol. Such moderate metastability is empirically supported by the multitude of frameworks accessible through relatively mild hydrothermal conditions.²⁵ Recent calorimetric studies were extended to the prototypical metal–organic framework, MOF-5.^{26,27} The measured energetic metastability of this MOF followed the trend established by the zeolitic and mesoporous materials while hinting at a diminishing destabilizing effect of decreasing density for highly porous materials.

This work reports measured energetics of several crystalline zinc ZIFs (ZIF-zni, ZIF-1, ZIF-4, ZIF-7, and ZIF-8) and the cobalt ZIF, CoZIF-4. These frameworks provide a large density range, as well as some variation in organic linker and framework topology (Figure 1). The as-synthesized (ZIF-4-DMF),

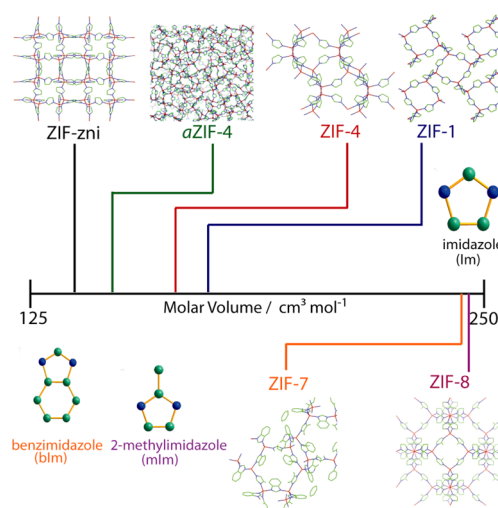


Figure 1. Topologies, imidazole linkers, and molar volume of studied ZIF materials.

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Table 1. Thermodynamic Cycle Used To Calculate Enthalpies of Formation of ZIF Frameworks from Dense Assemblages

reaction	enthalpy ^a
$\text{MO}(\text{cr}) + 2\text{H}^+(\text{aq}) \rightarrow \text{M}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{aq})$	$\Delta H_1 = \Delta H_f(\text{MO})$
$2[\text{H-Im}(\text{cr}) \rightarrow \text{Im}^-(\text{aq}) + \text{H}^+(\text{aq})]$	$\Delta H_2 = 2\Delta H_s(\text{H-Im})$
$x[\text{DMF}(\text{l}) \rightarrow \text{DMF}(\text{aq})]$	$\Delta H_3 = x\Delta H_s(\text{DMF})^b$
$\text{M}^{2+}(\text{aq}) + 2\text{Im}^-(\text{aq}) + x\text{DMF}(\text{aq}) \rightarrow \text{ZIF}(\text{cr})$	$\Delta H_4 = -\Delta H_s(\text{ZIF})$
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{aq})$	$\Delta H_5 = \Delta H_{\text{dil}}(\text{H}_2\text{O})$
$\text{MO}(\text{cr}) + 2\text{H-Im}(\text{cr}) + x\text{DMF} \rightarrow \text{ZIF}(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \Delta H_{\text{rxn}}$	$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_{\text{rxn}}$

^aAll ΔH_s values can be found in Table 2. ^bFor only ZIF-4-DMF, $x = 1.8$ DMF per formula unit. All other ZIF frameworks are fully evacuated.

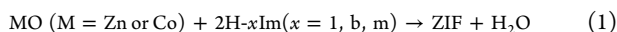
Table 2. Physical Properties and Thermodynamic Data of Materials Used in and Derived from Acid Solution Calorimetry^a

compd	formula	BET (m ² /g)	SAV (%)	FD (T/nm ³)	MV (cm ³ /mol T)	ΔH_s (kJ/mol)	ΔH_{rxn} (kJ/mol)	ΔH_{trans} (kJ/mol)	$\Delta H_f^{\circ}{}_{f,298\text{K}}$ (kJ/mol)
ZnO	ZnO					-72.29 ± 0.17			-350.5 ± 0.3^b
CoO	CoO					-105.82 ± 0.36			-237.9 ± 1.3^b
H-Im	C ₃ H ₄ N ₂					-35.72 ± 0.54			49.8 ± 0.6^c
H-mIm	C ₄ H ₆ N ₂					-43.08 ± 0.21			1.4 ± 0.8^d
H-bIm	C ₇ H ₆ N ₂					-19.49 ± 0.16			79.5 ± 1.3^c
H ₂ O	H ₂ O					-0.5^f			-285.83 ± 0.04^b
DMF	C ₃ H ₇ NO					-11.13 ± 0.33			-239.4 ± 2.49^e
ZIF-zni	Zn(Im) ₂	4	12	4.43	135.94	-109.62 ± 0.88	-33.62 ± 1.59	13.04 ± 2.54	1.31 ± 3.05
<i>a_m</i> ZIF-4	Zn(Im) ₂	10	23	4.08	147.60	-114.00 ± 0.52	-29.24 ± 1.23	17.42 ± 2.18	5.69 ± 2.69
ZIF-4-DMF	Zn(Im) ₂ ·1.8(DMF)		6.1	3.65	164.99	-135.65 ± 0.81	-27.63 ± 1.85	19.04 ± 2.80	-423.62 ± 7.79
ZIF-4	Zn(Im) ₂	300	34.3	3.65	164.99	-118.64 ± 1.05	-24.59 ± 1.76	22.07 ± 2.71	10.34 ± 3.22
CoZIF-4	Co(Im) ₂		36.2	3.65	164.99	-158.39 ± 0.80	-18.38 ± 1.70	28.28 ± 2.65	129.15 ± 4.16
ZIF-1	Zn(Im) ₂		33.9	3.46	174.05	-116.50 ± 0.84	-26.74 ± 1.55	19.92 ± 2.50	8.19 ± 3.01
ZIF-7	Zn(bIm) ₂		26.6	2.47	243.81	-91.28 ± 2.63	-19.48 ± 2.96	27.18 ± 3.91	74.85 ± 5.82
ZIF-8	Zn(mIm) ₂	1724	50.4	2.42	248.84	-138.36 ± 0.57	-19.59 ± 0.95	27.07 ± 1.90	-81.46 ± 2.81

^aBET, Brunauer–Emmett–Teller surface area; SAV, solvent-accessible volume; ⁵FD, framework density; MV, molar volume; ΔH_s , enthalpy of solution in 5 M HCl at 298 K; ΔH_{rxn} , enthalpy of formation from oxide and organic components presented in Table 2; ΔH_{trans} , coordination-corrected enthalpy of formation reaction (see text below); $\Delta H_f^{\circ}{}_{f,298\text{K}}$, standard enthalpy of formation from elements. ^bRef 28. ^cRef 29. ^dRef 30. ^eRef 31. ^fCalculated enthalpy of dilution of water in 5 M HCl.³²

evacuated (ZIF-4), and ball-milling amorphized phase (*a_m*ZIF-4) were each examined, providing quantitative energetics for the effects of solvent present in synthesis and of the framework amorphization.

A thermodynamic cycle (Table 1) and the solution enthalpies (ΔH_s , Table 2) were used to calculate the enthalpies of formation (ΔH_{rxn}) of the ZIFs plus liquid water from their crystalline dense components (metal oxide and imidazole linker, reaction 1):



The zinc-based frameworks have ΔH_{rxn} ranging from -33.6 to -19.6 kJ per mole of Zn. ZIF-zni is the densest known and most stable ZIF structure; thus it makes a convenient reference material to compare with other ZIFs having different M(Im)₂ structural building units (SBUs). A direct comparison can be made between our calorimetric results for ZIF-zni and ZIF-4 and the most recent, dispersion-corrected DFT calculations.⁷ Experiments reveal a difference in their heats of formation of 9.0 ± 3.4 kJ/mol, while van der Waals inclusive DFT calculations give the difference as 16.0 kJ/mol. Surprisingly, the agreement with the uncorrected DFT calculations is actually better (7.3 kJ/mol), with similar agreements seen for ZIF-1 as well.⁹ However, other aspects of the earlier calculations, in particular their poor agreement with experimental lattice parameters, indicate that the later calculations are more reliable, even though they appear to slightly overestimate the energetic destabilization resulting from dispersion interactions. The salient point is that both the

DFT calculations and calorimetric experiments suggest modestly increasing metastability with increasing porosity.

The 6.2 kJ/mol difference between CoZIF-4 and ZIF-4 is ascribed to the change in coordination of Co from octahedral in its oxide to tetrahedral in the ZIF-4 framework (SI-4). We also draw attention to the ΔH_{rxn} of the amorphous but relatively dense ZIF: *a_m*ZIF, which is destabilized by only 4.5 kJ/mol with respect to the dense phase ZIF-zni, a result that is reminiscent of the small enthalpy difference (9.0 kJ/mol) observed between silica glass and quartz.²⁰

The exothermic ΔH_{rxn} of the ZIFs from zinc oxide plus imidazole is consistent with experimental work which has shown that they can be synthesized at room temperature from ZnO plus the appropriate imidazole ligand by liquid-assisted grinding.³³ However, in analogy to comparing the energetics of porous silica phases to that of the dense polymorph, quartz, it is desirable to compare the energetics of porous ZIFs to a *hypothetical* dense ZIF analogue to obtain the destabilization resulting from an increase in porosity. The negative enthalpies of formation above include not only this destabilizing effect but also a stabilizing contribution from the change within the coordination sphere of the metal atom from oxygen to nitrogen in the formation reaction (eq 1). This exothermic effect is calculated to be -46.7 ± 1.0 kJ/mol (SI-3). Subtracting this correction from ΔH_{rxn} normalizes for this favorable effect and gives enthalpies (ΔH_{trans}) describing only the endothermic transition from the nonporous dense states to the open framework (Table 2). These corrected enthalpies show that,

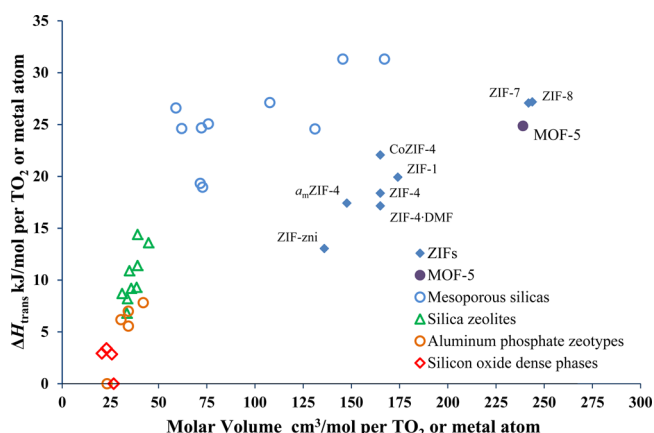


Figure 2. Enthalpy of silica dense phases,²⁰ silica zeolites,²¹ aluminum phosphate zeotypes,²² mesoporous silicas,^{24,25} and MOF-5¹² and ZIFs (corrected for O to N bonding change, ΔH_{trans}) with respect to dense assemblages.

despite the large molar volumes, the measured ZIFs are only moderately destabilized in enthalpy (13.0–27.1 kJ per mole of metal tetrahedra) compared to the hypothetical dense reference state defined above. The dispersion-corrected DFT calculations⁷ reveal that most of the destabilization of the porous ZIFs relative to the dense zni system is due to their lower dispersion interactions. The DFT calculations also confirm the constant geometry and interactions within the first coordination shell of the zinc ion bonded to nitrogen.

Thus the ZIFs and other classes of porous materials (mesoporous silicas, aluminophosphate zeotypes, siliceous zeolites, and MOF-5) reveal a rich energy landscape for a variety of materials which display only moderate destabilization with respect to their dense counterparts (Figure 2). The energetic trend (enthalpy vs molar volume) defined by the ZIFs parallels energetic findings of porous inorganic frameworks. Scatter within the data may reflect variations in bond type, bond angle, surface characteristics, linker functionalization, or other factors unique to each material. The slope of the porous inorganic plot in Figure 2 is initially steep, but becomes far less so beyond 65 cm³/mol. This is likely due to the diminishing loss of dispersive interactions as the structures become more open. It also reflects that the additional volume from the greater porosity creates space that is increasingly distant from any framework atoms, thus exerting a smaller influence on the framework. The trend for ZIFs and MOF-5 is similar to that for mesoporous silicas, but is displaced slightly downward toward smaller apparent destabilization for a given molar volume. This difference may reflect the difficulty in choosing an appropriate dense reference state material, uncertainty in making the oxygen to nitrogen bonding correction, or other chemical factors. There is no *a priori* reason to expect such a large variety of different chemistries and bond types to follow a single curve of energy versus volume. The important point is the overall similarity among these various classes of materials, namely only a modest increase of energy with molar volume which becomes less pronounced at high porosity.

These energetic findings are good news for the MOF and hybrid material communities, which have produced astoundingly porous MOFs^{34,35} and continue to seek pathways to create new highly porous functional materials.^{13,36,37} The data suggest that the thermodynamic stability of such ultraporous materials may become insensitive to void space. Thus, the limit

of void fraction that a MOF can encompass may be related to how far the limits of the union between a rigid linker and structural building units can be maximized, rather than to the porosity itself. Though eventual limits to how porous a MOF can be made are anticipated, what those limits actually are is not yet clear. The energetic trend in Figure 2 may break down at very high porosity, or MOFs of such high porosity may simply not exist, or may exist in solvated form only to collapse upon activation. Calorimetric studies of MOFs of higher porosity are in progress, though such MOFs are fundamentally different in structure and flexibility from the ZIFs studied here.

Calorimetry of the solvent-bearing ZIF, ZIF-4-DMF, showed the solvent interaction between the DMF and ZIF-4 framework to be minor, −3.0 kJ per mole of Zn, mirroring the mild solvent interactions seen in other porous systems.^{22,25,26} This suggests that solvent passively fills void space in the final framework, though it may play a more specific role stabilizing intermediates during crystallization.³⁸ Mechanical studies also support this, showing DMF solvent in ZIF-8 to contribute only 3–6% to the stiffness of the framework. The weak interactions between solvent and structure imply that, as the void space increases, one must focus upon robust linker–metal interactions to prevent framework collapse and retain structural porosity.

ZIFs become energetically less stable with increasing porosity, but the degree of weakening becomes smaller as the void volume increases, suggesting that large voids begin to act like a second phase with little additional destabilization. The trend for ZIF materials overlaps with MOF-5, demonstrating that the metastability of MOF-5 is not an anomaly, but rather a portion of a larger trend for porous hybrid materials. The energetics of this trend parallel the metastability curve established by zeolites, zeotypes, and mesoporous silicas. The variation with density of measured enthalpies agrees qualitatively with values predicted by DFT calculations.

■ ASSOCIATED CONTENT

● Supporting Information

Sample preparation, characterization data, solution calorimetry methods, and coordination correction calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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