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Thermodynamics of solvent interaction with the metal–organic framework MOF-5

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The inclusion of solvent in metal–organic framework (MOF) materials is a highly specific form of guest–host interaction. In this work, the energetics of solvent MOF-5 interactions has been investigated by solution calorimetry in 5 M sodium hydroxide (NaOH) at room temperature. Solution calorimetric measurement of enthalpy of formation (ΔH_f) of $Zn_4O(C_8H_4O_4)_3{\cdot}C_3H_7NO$ (MOF-5·DMF) and $Zn_4O(C_8H_4O_4)_3{\cdot}0.60C_5H_{11}NO$ (MOF-5·0.60DEF) from the dense components zinc oxide (ZnO), 1,4-benzenedicarboxylic acid (H_2BDC), *N*,*N*-dimethylformamide (DMF) and *N*,*N*-diethylformamide (DEF) gives values of 16.69 ± 1.21 and 45.90 ± 1.46 kJ (mol Zn_4O)$^{-1}$, respectively. The enthalpies of interaction (ΔH_{int}) for DMF and DEF with MOF-5 are −82.78 ± 4.84 kJ (mol DMF)$^{-1}$ and −89.28 ± 3.05 kJ (mol DEF)$^{-1}$, respectively. These exothermic interaction energies suggest that, at low guest loading, Lewis base solvents interact more strongly with electron accepting Zn_4O clusters in the MOF than at high solvent loading. These data provide a quantitative thermodynamic basis to investigate transmetallation and solvent assisted linker exchange (SALE) methods and to synthesize new MOFs.

1. Introduction

The synthesis of metal–organic frameworks (MOFs) has attracted immense attention during the last two decades due to the ability to obtain a large variety of scientifically interesting highly porous structures that could have applications for gas storage, separations, catalysis, and sensors, based on the pore size and shape as well as the host–guest interactions involved.[1–7] Although a myriad of MOFs has been reported, numerous predicted structures are yet to be prepared experimentally.[1–7] To circumvent kinetic and/or thermodynamic limitations of direct techniques, innovative synthetic routes such as solvent assisted linker exchange (SALE) and transmetallation are indispensable.[8–10] By using these techniques, previously unobtainable MOFs (*e.g.* metastable MOF-5 analogues, Cd–ZIFs) have been prepared.[8,10] One of the most crucial parameters in all these strategies, including hydro/solvothermal, SALE, and transmetallation, is solvent.[8–10] During the synthesis, depending on the nature of solvent, various intermediate structures may form and solvent might direct overall reaction to different products.

Recently, it was reported that Zn^{2+} ions of $Zn_4O(C_8H_4O_4)_3$ (MOF-5) (Fig. 1) bind solvent molecules, thereby converting MOF-5, previously believed to be a robust structure, into a dynamic system that incorporates intricate host–guest interactions.[10] Comprehension of dynamic solvent–MOF-5 binding allowed synthesis of previously the unattainable metastable $ZnCo_3O(C_8H_4O_4)_3$ structure through transmetallation.[10] However, previous thermochemical investigations on MOF-5 with excess DEF loading suggest very weak solvent–MOF interactions (−5.2 ± 1.6 kJ (mol of Zn·DEF)$^{-1}$) and that solvent acts largely as space filler and hence there is no genuine bond between DEF and MOF-5.[11] Nevertheless, in that report, due to the excess loading of guest molecules, the measured energetic values might have included not only DEF–MOF interactions but also solvent–solvent interactions in the interface and void space of the MOF. Therefore, in the present study, to determine the energetics of solvent–Zn_4O binding, MOF-5 samples with low guest contents (MOF-5·1.0DMF and MOF-5·0.60DEF, see Fig. 3) were prepared.

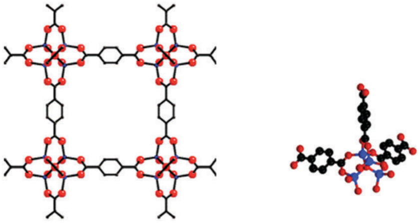

Fig. 1 Crystal structure and secondary building unit of MOF-5. C, O, and Zn are shown in black, red, and dark blue colors. H-atoms are omitted for clarity.

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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 DMF(DEF)) *via* room-temperature solution calorimetry in 5 M NaOH

Reaction scheme	Enthalpy measurement
$4Zn^{2+}(aq) + 3BDC^{2-}(aq) + DMF(0.60DEF)(aq) + 2OH^-(aq) \rightarrow Zn_4O(BDC)_3\cdot DMF(0.60DEF)(cr) + H_2O(l)$	$\Delta H_1 = -\Delta H_s(\text{MOF-5})$
$4(ZnO(cr) + H_2O(aq) \rightarrow Zn^{2+}(aq) + 2OH^-(aq))$	$\Delta H_2 = \Delta H_s(ZnO)$
$3(H_2BDC(cr) + 2OH^-(aq) \rightarrow BDC^{2-}(aq) + 2H_2O(aq))$	$\Delta H_3 = \Delta H_s(H_2BDC)$
$DMF(0.60DEF)(l) \rightarrow DMF(0.60DEF)(aq)$	$\Delta H_4 = -\Delta H_s(DMF(DEF))$
$3(H_2O(aq) \rightarrow H_2O(l))$	$\Delta H_5 = -\Delta H_{dil}(H_2O)$
$4ZnO(cr) + 3H_2BDC(cr) + xDMF(yDEF)(l) \rightarrow Zn_4O(BDC)_3DMF(0.60DEF) + 3H_2O(l)$	$\Delta H_{rxn} = \Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

Table 2 Thermodynamic data for materials used in and derived from solution calorimetry. (5 M NaOH at room temperature)

Compound	Formula	ΔH_s (kJ (mol $Zn_4O)^{-1}$)	ΔH_{rxn} (kJ (mol $Zn_4O)^{-1}$)	ΔH_f (kJ (mol Zn$)^{-1}$)
ZnO	ZnO	-0.34 ± 0.28[a]		
H_2BDC	$C_8H_6O_4$	-70.07 ± 0.12[a]		
DEF	$C_5H_{11}NO$	-4.30 ± 0.01[a]		
DMF	C_3H_7NO	-0.48 ± 0.06		
H_2O	H_2O	0.5[a]		
MOF-5·0.60DEF	$(Zn_4O)(C_8H_4O_4)_3\cdot 0.60C_5H_{11}NO$	-258.55 ± 1.33	45.90 ± 1.46	11.48 ± 0.37
MOF-5·DMF	$(Zn_4O)(C_8H_4O_4)_3\cdot C_3H_7NO$	-227.24 ± 1.05	16.69 ± 1.21	4.17 ± 0.30
MOF-5	$(Zn_4O)(C_8H_4O_4)_3$	-309.55 ± 5.09[a]	99.47 ± 3.62	24.87 ± 0.91

[a] Ref. 11.

Some thermodynamic terms used in this work are defined below. The solution enthalpy (ΔH_s) represents the energy released or absorbed when the sample pellet dissolves in the solvent (5 M NaOH, at 25 °C).[11,12] By using a thermodynamic cycle (Tables 1 and 2) based on Hess's law and state function properties of enthalpy, the ΔH_s of each step was used to determine the enthalpy of reaction (ΔH_{rxn}), namely the enthalpy of formation (ΔH_f) of MOF from ZnO, organic linker and solvent. Additionally, the interaction enthalpy (ΔH_{int}), which represents the binding strength of molecules (DMF/DEF) with MOF-5, was derived by taking differences of ΔH_f of activated (solvent-free) MOF-5 and DMF/DEF occluded MOF-5.

2. Experimental methods

(a) Synthesis

Zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6(H_2O)$) (0.446 g, 2.355 mmol) and 1,4-benzenedicarboxylic acid (0.083 g, 0.499 mmol) were dissolved in 49 mL of anhydrous *N*,*N*-dimethylformamide (DMF) and 1 mL of deionized water in a 100 mL jar with a Teflon cap. These contents were added to an oven preheated to 100 °C and kept there for 7 h. After cooled to room temperature, the crystals were collected by gravity filtration under an inert atmosphere of N_2 in a bench top glovebag. They were transferred under N_2 to a N_2-filled glovebox and washed six times with fresh DMF, waiting 8 h between each wash, and then with di-chloromethane (CH_2Cl_2) in a similar manner. The solid was collected by gravity filtration and heated to 180 °C for 12 h under 10^{-5} torr pressure. 25 mg of fully evacuated MOF-5 was suspended in 5 mL of DMF/DEF and left for at least 12 h. The DMF/DEF was replaced by 20 mL of CH_2Cl_2, left for 8 h, then solvent was replaced two more times. The resulting crystals were placed under reduced pressure at room temperature for several hours with no additional heating.

(b) Thermogravimetric analysis (TGA)

All TGA experiments were performed on a Netzsch STA 449 system from 30 °C to 550 °C at 5 °C min^{-1} under Ar gas flow.

(c) Solution calorimetry

Solution enthalpies were measured with a CSC (Calorimetry Sciences Corporation) 4400 isothermal microcalorimeter (Fig. 2) operating at 25 °C following the method described by Hughes *et al.*[11] For each measurement, 25.0 g of 5 M NaOH was placed inside a 50 mL teflon cell that is part of a removable apparatus that allows placement of the solvent into the calorimeter. A calorimetry experiment consisted of dropping a pellet (~5 mg) into isothermally equilibrated NaOH aqueous solution (5 M). Each pellet was prepared in an argon filled glovebox and weighed using a Mettler microbalance with an accuracy of 1 μg. After each experiment the cell was reassembled with fresh solvent and equilibrated with the isothermal block over six hours in the calorimeter before performing the next measurement.

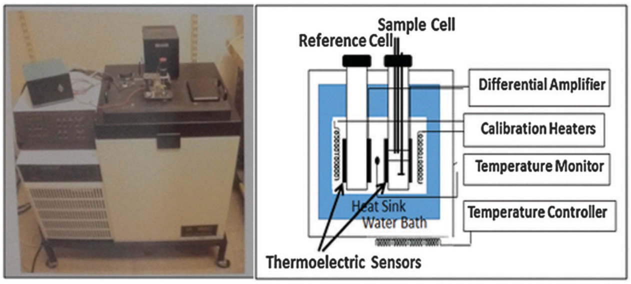

Fig. 2 CSC 4400 isothermal microcalorimeter and its schematic.

The calorimetric cell was connected to the outside environment by a 5 mm inner diameter silica glass tube approximately 1 m in length. Liquid DMF was injected through a teflon tube that extended through the silica connection tube to approximately 2 cm above the solvent surface. The mass of injected DMF was determined by weighing the syringe assembly before and after DMF injection. The dry masses of the syringe and Teflon tube were known, allowing the amount of DMF injected into the calorimetric cell to be calculated. All the weight measurements involving DMF were done on a Mettler microbalance with an accuracy of 10 μg. Mechanical stirring at approximately $\frac{1}{2}$ Hz was applied to all experiments. After each experiment the cell was removed, reassembled with fresh solvent, and reequilibrated in the calorimeter for at least 6 hours before the next measurement. For each sample, we performed 4–6 measurements and took their average as the final value. The uncertainty reported in each enthalpy represents the 95% confidence interval. The calorimeter was calibrated by dissolving 15 mg pellets of NIST standard reference material KCl in 25 g of water, which corresponds to a reference concentration of 0.008 mol kg^{-1} at 25 °C. The calibration factor was calculated using the known solution enthalpy for the reference concentration of 0.008 mol kg^{-1} and enthalpy of dilution measurements. The total heat effect due to sample dissolution was obtained by integrating the calorimetric signal with a linear baseline, which was then converted to joules, using the calibration factor obtained using KCl. This methodology has been described previously.[11,12]

3. Results and discussion

To confirm single phase and composition, MOF-5 samples were analyzed by powder X-ray diffraction and TGA, see Fig. 3. Both samples have X-ray diffraction patterns similar to that of MOF-5 reported in the literature.[13] Sample compositions were evaluated from TGA results as MOF-5·1.0DMF and MOF-5·0.60DEF.

Using a thermodynamic cycle (Table 1) and the measured solution enthalpy (ΔH_s) (Table 2), the enthalpies of formation (ΔH_f) of MOF-5·1.0DMF and MOF-5·0.60DEF from their dense phase assemblages, zinc oxide (ZnO), H_2BDC, DMF, and DEF, have been determined. These values are 16.69 ± 1.21 and 45.90 ± 1.46 kJ (mol $Zn_4O)^{-1}$ for MOF-5·1.0DMF and MOF-5·0.60DEF, respectively, while the ΔH_f of activated (solvent free) MOF-5 is 99.47 ± 3.62 kJ (mol $Zn_4O)^{-1}$.[11] These results show that both the solvated and the activated MOF-5 samples are energetically metastable with respect to their dense phase assemblages. Incorporation of solvent diminishes but does not eliminate the energetic metastability.

The enthalpies of interaction of DMF and DEF with the Zn_4O node in MOF-5 are −82.78 ± 4.84 kJ (mol DMF)$^{-1}$ and −89.28 ± 3.05 kJ (mol DEF)$^{-1}$. Note that in the thermodynamic cycles and calculated enthalpies of interaction, the standard state for solvent (DEF/DMF) is liquid (not gas/vapor). On the other hand, the enthalpies of interaction are −129.68 ± 4.84 kJ (mol DMF)$^{-1}$ and −139.58 ± 3.05 kJ (mol DEF)$^{-1}$ if we choose gas/vapor as reference state.[14] The interaction enthalpy values reported in this work are much more exothermic than that reported for high solvent loading in MOF-57.4DEF, namely −20.8 ± 6.4 kJ (mol DEF)$^{-1}$ (multiplied by 4 to obtain DEF–Zn_4O energy in kJ (mol DEF)$^{-1}$ instead of DEF–Zn interaction in kJ (mol Zn·DEF)$^{-1}$).[11] The enthalpy at low solvent loading represents mainly direct solvent–MOF interactions, while at excess loading, both guest–host and guest–guest (solvent–solvent) interactions compete in an intricate and balanced manner.[15,16]

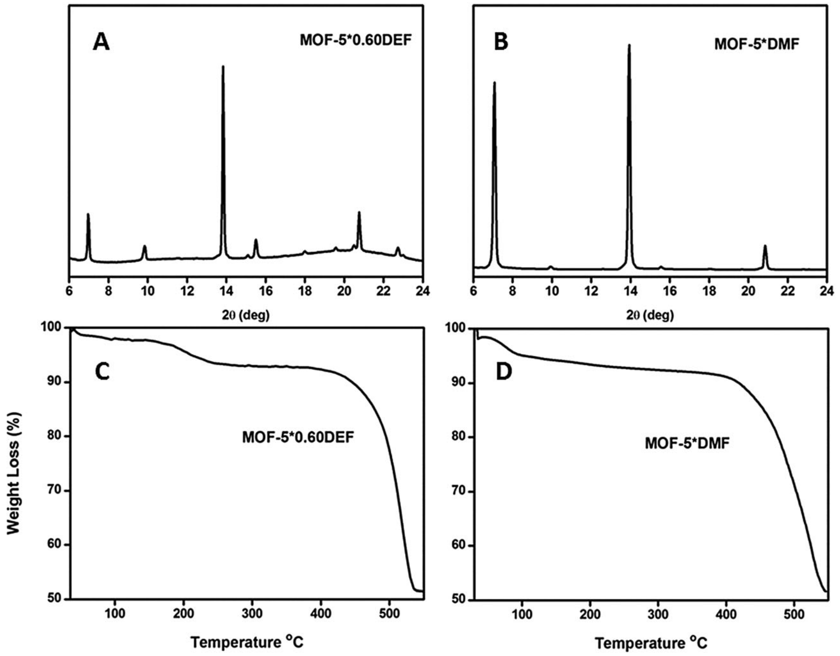

Fig. 3 Powder X-ray diffraction and TG analysis of MOF-5·DMF (B and D, respectively) and MOF-5·0.6DEF (A and C, respectively).

The 4-fold increase in heat of binding of DMF/DEF–MOF-5 at low solvent loading could be attributed to the energetics of solely guest–host interactions, whereas at high solvent loading, weaker guest–guest interactions may contribute to the overall enthalpy, making the average value smaller in magnitude. Indeed if one recalculates the interaction enthalpy in MOF-57.4DEF as coming only from the first 0.6 moles of solvent, as in the present report, one gets an interaction enthalpy of *ca.* -256 kJ (mol DEF)$^{-1}$. This is more exothermic by almost a factor of three than the measured enthalpy in this work, suggesting either that more than 0.6 moles of solvent have strong interactions with the framework, or that the solvent–solvent interactions are substantially stronger under confinement than in pure DEF. At present these two possibilities cannot be separated. Furthermore, the magnitudes of binding enthalpies of DMF/DEF–MOF-5 reported here reinforce that Zn_4O nodes form true chemical bonds with solvent molecules.[10] These calorimetric findings confirm that not all the solvent in MOF-5 acts just as a void filler by showing that, for low loading, DMF/DEF bonds strongly with MOF-5 and therefore can play a significant thermodynamic role in dynamic behavior of Zn_4O nodes.[10,11]

At low solvent loading, the magnitude of interaction enthalpies is primarily determined by the specific binding between the secondary building unit of the MOF and the solvent. Consequently, the chemical nature (Lewis acidity/basicity, molecular geometry, functionalities, *etc.*) of building units of MOFs and solvents modulate the strength of guest–host interactions. Since MOF-5 is built from Lewis acidic Zn_4O nodes interconnected with 1,4-benzenedicarboxylates, the very negative binding energetics of Lewis basic DMF and DEF to the acidic zinc centers is reasonable.[17] Furthermore, DEF shows slightly more exothermic interaction energy (stronger bonding) than DMF. As shown by computational and experimental data, the resonance structures of DMF and DEF interact with $M_2(O_2C)_4$ clusters of copper and zinc based paddle-wheel MOFs through their carbonyl oxygens.[18,19] Owing to similar acidic nature of Zn_4O nodes, it might be deduced that both solvents bind to MOF-5 *via* carbonyl moieties. The strongly electron withdrawing nature of the carbonyl group by resonance allows delocalization of the non-bonded electrons of nitrogen. Due to better electron donating properties of C_2H_5 groups than of CH_3, DEF has a more stable resonance form and stronger Lewis basicity than DMF. Comparison of donor numbers (DN), which is a quantitative measure of Lewis basicity, of DMF (111.1 kJ mol^{-1}) and DEF (129.1 kJ mol^{-1}) also supports that DEF has slightly higher basicity.[20] These properties result in a more exothermic binding enthalpy in DEF–MOF-5 than in DMF–MOF-5.

In a study of I_2 interaction with ZIF-8 at low guest loading (0.59 I_2 per ZIF-8), the binding energy of I_2–ZIF-8 was also found to be highly exothermic (-41.5 ± 2.0 kJ (mol of $Zn\cdot I_2$)$^{-1}$).[21] This strong guest–host interaction was attributed to the formation of electron donor–acceptor complexes between the imidazole of ZIF-8 and I_2 and to negligible I_2–I_2 intermolecular interactions. These calorimetric studies emphasize that guest–host interactions are driven primarily by the electron donating–accepting nature of the framework and guest molecule and the level of guest coverage.

Finally, it was found in studies of mechanisms of transmetallation of MOF-5 lattices that both in associative and dissociative paths, the strength of the metal–solvent bond is the main descriptor of kinetics (*i.e.* rate constants).[9] Particularly, it was demonstrated that, for several metals (Co, Fe, Cr, Mn, Ti, V, Ni) and solvents (DMF, tetrahydrofunran (THF), dimetylsulfoxide (DMSO), acetonitrile (MeCN)), the extent of incorporation of metals in the MOF-5 structure depends on metal–solvent interaction enthalpy obtained by DFT calculations.[9,22] The current measurement of DEF–MOF-5 and DMF–MOF-5 interaction energies may thus validate the computational predictions and give insight into transmetallation and SALE techniques by quantifying experimentally the sensitivity of interaction enthalpies to Lewis acidity/basicity and solvent coverage. Therefore, we propose that by meticulously designing and engineering specific molecule–MOF interactions with unique interaction energies, it may be possible to synthesize unprecedented MOF structures through post-synthetic methods, as already demonstrated for metastable Co–MOF-5.[10]

4. Conclusion

Calorimetric studies of interactions between different solvents and MOF-5 have been performed. At low solvent loading, the enthalpies of DMF/DEF–MOF-5 binding are much more exothermic than those at much higher solvent loading for DEF. We conclude that the enthalpies of guest–host interactions in MOFs are largely controlled by the electron accepting–donating (acid–base) characteristics.

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