REVIEW ARTICLE

Recent advances in experimental thermodynamics of metal–organic frameworks

Hui Sun,[1,2] and Di Wu [ORCID][3,4,5,6,a)]

[1]*Petroleum Processing Research Center, East China University of Science and Technology, Shanghai 200237, China*
[2]*International Joint Research Center of Green Energy Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China*
[3]*Alexandra Navrotsky Institute for Experimental Thermodynamics, Washington State University, Pullman, Washington 99163, USA*
[4]*The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99163, USA*
[5]*Department of Chemistry, Washington State University, Pullman, Washington 99163, USA*
[6]*Materials Science and Engineering, Washington State University, Pullman, Washington 99163, USA*

This mini review summarizes recent advances in experimental thermodynamics of metal–organic frameworks (MOFs). Taking advantage of the development in mechanochemistry, near-room temperature solution calorimetry, and low-temperature heat capacity measurements, the energetic landscape, entropy trends, and Gibbs free energy evolutions of MOFs with true polymorphism [$Zn(MeIm)_2$, $Zn(EtIm)_2$, and $Zn(CF_3Im)_2$] as framework topology varies were thoroughly explored by integrated calorimetric and computational methodologies. In addition, the formation enthalpies of MOFs with ultrahigh porosity (*MOF*-177 and *UMCM*-1) and the simplest structure (*metal formates*) have been determined. The studies summarized below highlight the complex interplays among interrelated compositional, chemical, and topological (structural) factors in the determination of the thermodynamic parameters of MOFs. © 2019 International Centre for Diffraction Data.
[doi:10.1017/S0885715619000782]

I. INTRODUCTION

Metal–organic frameworks (MOFs) are a family of hybrid porous materials with high surface areas constructed by the coordination of metal nodes and organic linker molecules (Cook *et al*., 2013). Owing to their unique chemical, compositional, and structural properties, they have promising application potential serving as sorbents, catalysts, sensors, and drug-loading hosts (Furukawa *et al*., 2013; Li *et al*., 2017). Although there are a significant number of publications on characterizations and functionalities of MOFs during the past decade, the thermodynamics of MOFs are underexplored (Wu and Navrotsky, 2015), especially considering the rapid growth of newly synthesized MOF structures. Recent advances in material synthesis techniques, such as mechanochemical approaches, enable the synthesis of isocompositional MOFs with different framework topologies, for further exploration of thermodynamics of true polymorphs. Additionally, the successful synthesis of MOFs with ultrahigh porosity and the simplest metal formate structures help us to push the limits at both ends to further our understanding of the energetic landscape of porous materials.

In this mini review, we summarize recent advances in experimental thermodynamic studies on MOFs. The studies highlighted here were primarily carried out by our colleagues in the Friščić group at McGill University (mechanochemical

synthesis), the Navrotsky group at University of California, Davis (energetic stability), and the Woodfield group at Brigham Young University (heat capacity). Specifically, *near-room temperature solution calorimetry* with different solvents and *low-temperature heat capacity measurements* were integrated to reveal the enthalpy, entropy, and free energy evolutions for MOFs with ultrahigh porosity, simplest structure, and true polymorphism. In addition, from a chemical engineering perspective, we briefly introduce the ongoing research on molecular guest–MOF interactions in the Sun group at the East China University of Science and Technology and the Wu group at Washington State University, in which we performed a series studies using MOF as sorbents for adsorptive separation of petroleum compounds, such as alkane/alkene mixtures and organosulfur species (Sun *et al.*, 2019a, 2019b).

II. FRAMEWORK ENERGETICS – "PUSHING THE LIMITS TO BOTH SIDES: ULTRAHIGH POROUS AND THE SIMPLEST MOFs"

A. Thermodynamic penalty of ultraporous MOFs

The energetic stability of several representative MOFs, including MOF-5, HKUST-1, and zinc zeolitic imidazolate frameworks (ZIFs), has been studied and reviewed earlier (Wu and Navrotsky, 2015). Generally, as the molar volume increases, MOFs tend to be energetically less stable. To explore the potential limit of thermodynamic stability of MOFs as a function of molar volume, in 2015, Akimbekov
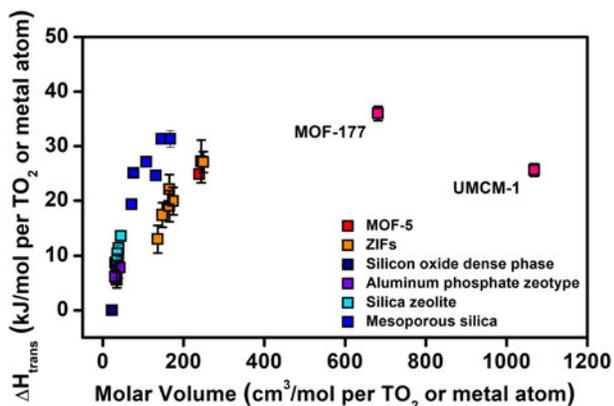
Figure 1. (Colour online) Energy landscape of inorganic and hybrid porous materials with respect to their corresponding dense assemblages. "T" represents a T-atom in the zeolite frameworks or ZIFs, which is tetrahedrally coordinated. Reprinted with permission from (Wu and Navrotsky, 2015). Copyright 2015 Elsevier. (Akimbekov and Navrotsky, 2016). Copyright 2016 John Wiley & Sons.

et al. used *acid solution calorimetry* to measure the formation enthalpies of two MOFs with ultrahigh porosity, MOF-177 (681.7 cm^3 per mole of Zn) and UMCM-1 (1068.3 cm^3 per mole of Zn) (Akimbekov and Navrotsky, 2016). These ultra-porous MOFs have molar volume more than 10 times higher than their corresponding dense phases. The calorimetric results suggest that despite the significantly high molar volume, the formation enthalpies of ultraporous MOF-177 and UMCM-1 fall in the same range with other MOFs with much less porosity, 7–36 kJ per mole of metal. These formation enthalpy results strongly suggest that the energetic cost of being ultrahigh porous for MOFs is relatively small (see Figure 1). In other words, MOF materials with extremely high surface area and ultrahigh porosity are thermodynamically feasible to access. This is good news for chemists and materials scientists who aim to design and synthesize such materials.

B. Energetic stability of the simplest MOFs: metal formates

Metal formates, $[M(HCOO)_2] \cdot xH_2O,$ are considered as MOFs with the simplest compositions and structures, in which metal cations, such as Li^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, are coordinated with formate anions. Metal formates have great potential to be applied as lithium-ion battery materials and gas adsorption or storage sorbents. Nagabhushana *et al.* (2018) measured the formation enthalpies of a series of metal formates with *acid solution calorimetry.* Specifically, the formation of metal formates from their dense phase assemblages, either metal oxides or chlorides and formic acid, is energetically favorable. The thermodynamic stability of metal formates decreases following the order of $Mg^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Li^+$, spanning from −119 to −34 kJ per mole of metal from oxides, and from −91 to −20 kJ per mole of metal from chlorides. The enthalpy of transition from dense phase is not discussed as a function of molar volume, since variation in metal type does not significantly modify the molar volume of metal formates.

C. Thermodynamic stability of MOFs with true polymorphs

ZIFs are formed by the coordination between metal nodes and imidazole linkers. Interestingly, once mechanically milled, some ZIFs were found to have true polymorphs (iso-compositional) with the same chemical composition are yet denser and energetically more stable. In 2017, using *solution calorimetry* and periodic density functional theory (DFT) calculations as the fundamental tools, Akimbekov *et al.* (2017) reported the first integrated calorimetric and computational study on the relative energetic stabilities of isocompositional MOFs exhibiting true polymorphism as ligand and framework topology vary. Specifically, in their study, two families of ZIFs with distinct polymorphs, such as zeolite RHO (RHO), analcime (ANA), β-quartz (qtz), sodlite (SOD), katsenite (kat) and diamondoid (dia), were synthesized with either 2-methylimidazolate (MeIm) or 2-ethylimidazolate (EtIm) as linkers. The calorimetric measurements and DFT modeling results suggest a clearly defined relationship between the energetic stability (formation enthalpies) of MOFs and their densities (Figure 2). Additionally, it is also found that ligand substituent has a significant impact on the energetic stability of these ZIFs, in which ethyl groups in $Zn(EtIm)_2$ are found to energetically stabilize ZIFs more compared with the methyls of $Zn(MeIm)_2$ (see Figure 2 for magnitudes in enthalpy). Moreover, they also demonstrate that ZIFs obtained from mechanochemical synthesis and/or transformation follow the general principle of Ostwald's rule with stagewise topological transitions toward reaching energetically more stable dense phases.
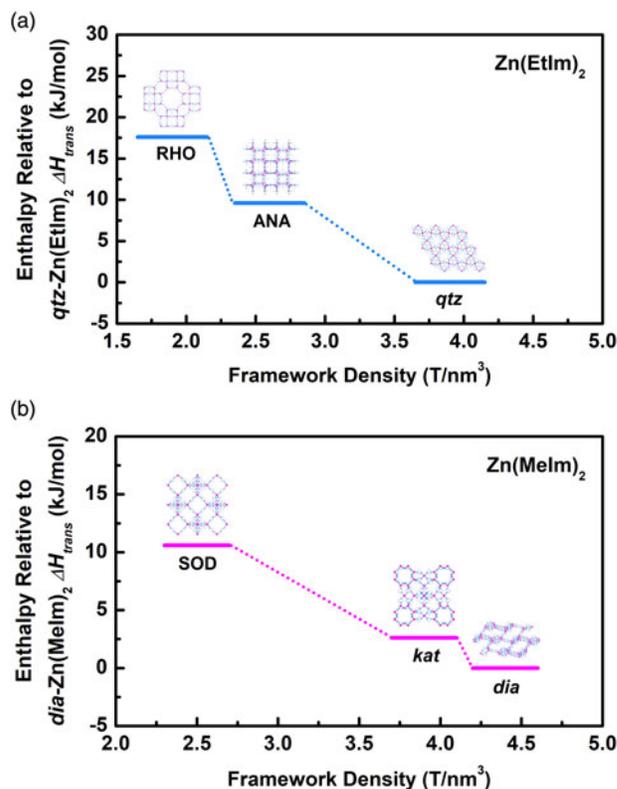

Figure 2. (Colour online) The measured enthalpy of transition relative to the corresponding polymorph with the highest density versus the framework density: (a) $Zn(EtIm)_2$ and (b) $Zn(MeIm)_2$. Reprinted with permission from (Akimbekov *et al.*, 2017). Copyright 2017 American Chemical Society.
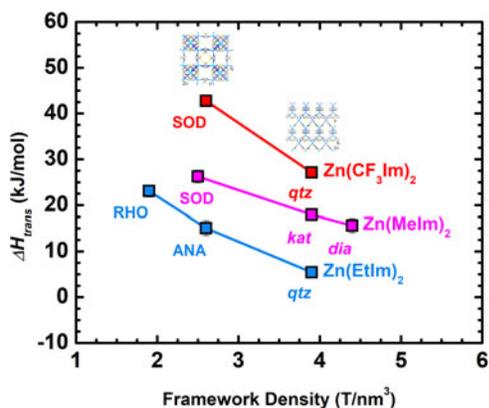
Figure 3. (Colour online) Enthalpies of transition, ΔH_{trans}, for true polymorphs of $Zn(MeIm)_2$ (pink), $Zn(EtIm)_2$ (blue), and $Zn(CF_3Im)_2$ (red). The topology of each sample is labeled. Reprinted with permission from (Arhangelskis et al., 2019). Copyright 2019 American Chemical Society.
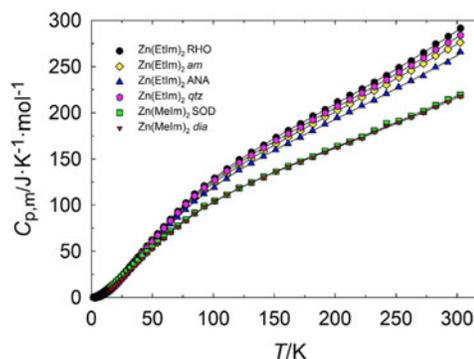

Figure 4. (Colour online) Molar heat capacity at constant pressure as a function of the temperature of SOD- and dia-polymorphs of $Zn(MeIm)_2$, and RHO-, ANA-, qtz-, and amorphous polymorphs of $Zn(EtIm)_2$. Reprinted with permission from (Calvin et al., 2018; Rosen et al., 2019). Copyright 2019 Elsevier.

D. Topological landscape and energetic stability of a fluorinated ZIF, $Zn(CF_3Im)_2$: theoretical prediction vs. experimental validation

Using dispersion-corrected periodic DFT as the theoretical approach, Arhangelskis et al. predicted the preferred topologies and the stability of different polymorphs of ZIFs, a family of MOFs with rich topological and energetic landscapes (Arhangelskis et al., 2019). Further, they employed mechanochemical synthesis and *acid solution calorimetry* measurement to validate their prediction. Specifically, in their DFT prediction, a series of hypothetical structures of a fluorinated ZIF, $Zn(CF_3Im)_2$, with distinct topologies (SOD and dia), were constructed and ranked in energy. Subsequently, mechanochemical screening and calorimetric evaluation were carried out, in which two-thirds of the predicted topologies, including a fluorinated ZIF-8 analog, were found to match well with experimentally synthesized samples possessing identical structures and energetic differences (see Figure 3). This study points out that dispersion-corrected periodic DFT is an effective methodology to predict both topological and energetic landscapes of ZIFs and MOFs in general.

III. HEAT CAPACITY AS A FUNCTION OF TEMPERATURE

A. Heat capacity of MOFs with true polymorphs: $Zn(EtIm)_2$ and $Zn(MeIm)_2$

Calvin et al. (2018) reported the first experimental thermodynamics studies on constant pressure heat capacities on ZIFs with different topologies, including RHO, ANA, and qtz, and the amorphous form of $Zn(EtIm)_2$ obtained by mechanochemical milling. Specifically, they measured the molar heat capacities from 1.8 to 300 K using *a Quantum Design Physical Property Measurement System (PPMS)*. Subsequently, the heat capacity data were fitted using (i) integrated theoretical functions below 15 K, (ii) orthogonal polynomials between 10 and 60 K, and (iii) a combined Debye and Einstein functions at temperatures above 50 K. The calculated $C_{p,m}°$, $\Delta_0 TS_m°$, $\Delta_0 TH_m°$, and $\Phi_m°$ data were plotted as a function of temperature between 0 and 300 K

(see Figure 4). Interestingly, although variation in heat capacities mirroring their specific structures were found for these ZIFs, a shared unique heat capacity feature was observed at about 100 K for all samples. This phenomenon is very likely to be chemically determined by the vibrational behaviors of metal nodes, linkers, and/or structural building units shared by these topologies. In general, for the topologies of $Zn(EtIm)_2$ investigated, the entropies of transition are much more complex than the enthalpies of transition, which is a relatively simple function of molar volume (density). It is very interesting to find the Gibbs free energies of the three energetically less stable polymorphs, ANA, RHO, and amorphous RHO, appear to be quite similar (see Figure 4).

Very recently, Rosen et al. reported a study using both *low-temperature heat capacity* and *inelastic neutron scattering (INS)* to reveal the energetics–structure relations of sodalite (SOD) and diamondoid (dia) topologies for zinc 2-methylimidazolate, $Zn(MeIm)_2$ (Rosen et al., 2019). Specifically, the molar heat capacities were measured directly between 1.8 and 300 K, followed by theoretical fitting and determination of $C_{p,m}°$, $\Delta_0 TS_m°$, $\Delta_0 TH_m°$, and $\Phi_m°$. The difference in Gibbs free energy corresponding to the phase transition from SOD to dia topology is -4.6 ± 2.2 kJ per mole of $Zn(MeIm)_2$, which suggests the phase transition between SOD and dia topologies is primarily driven by enthalpy factors. Interestingly, unlike $Zn(EtIm)_2$, the heat capacity of $Zn(MeIm)_2$ does not have a clear dependence on density. For $Zn(EtIm)_2$, the denser dia topology shows a lower heat capacity value compared with that of SOD at a particular temperature (see Figure 4). Moreover, there appears to be no transition for the heat capacity plots of $Zn(MeIm)_2$ throughout the whole temperature range. This observation strongly supports that the transition seen at about 100 K for $Zn(EtIm)_2$ can be attributed to the ethyl group of 2-ethylimidazole linker molecules. On the other hand, the presence of low-energy modes is experimentally confirmed by *INS spectroscopy*, which strongly suggests that the observed higher low-temperature heat capacity (higher entropy) of energetically less favorable SOD topology is mainly due to the dynamics of methyl groups on the imidazolate linkers. In addition, the *INS* data suggest the existence of low-energy modes evidenced by the gapped term of the fitted data of SOD and dia topologies at low temperature.
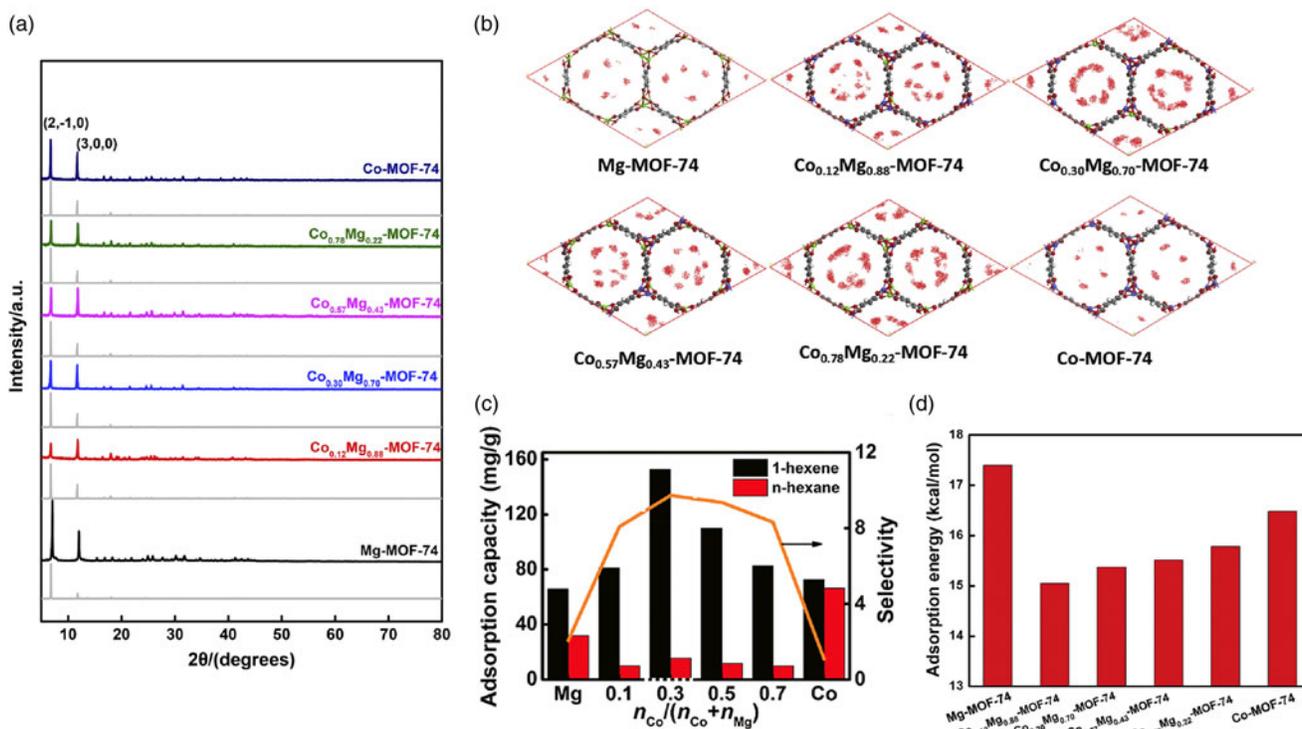
Figure 5. (Colour online) (a) Powder X-ray diffraction patterns of Co_xMg_{1-x}–MOF-74. (b) Equilibrium structures of 1-hexene adsorption on Co_xMg_{1-x}–MOF-74. (c) 1-hexene and n-hexane adsorption capacities and selectivity on Co_xMg_{1-x}–MOF-74. (d) Calculated adsorption energies of 1-hexene on Co_xMg_{1-x}–MOF-74. Reprinted with permission from (Sun *et al.*, 2019b). Copyright 2019 Elsevier.

IV. ADSORPTION SEPARATION OF LIQUID-PHASE ALKANE/ALKENE MIXTURES USING MOFs

A. Bimetallic Co_xMg_{1-x}–MOF-74 for 1-hexene/n-hexane separation – the critical role of metal sites

Sun *et al.* (2019b) synthesized a series of bimetallic, Co_xMg_{1-x}–MOF-74 ($x = 0$–1.0) using a facile solvothermal method. The samples were thoroughly characterized by XRD, N_2 adsorption, TG-DSC, SEM, EDS, FT-IR, and XPS. The powder X-ray diffraction data strongly suggest that all Co_xMg_{1-x}–MOF-74 samples are isostructural [see Figures 5(a) and 5(b)]. Subsequently, the 1-hexene/n-hexane adsorption capacity and selectivity were evaluated using static adsorption, in which significantly enhanced adsorption capacity and selectivity for 1-hexene molecules were observed. Particularly, $Co_{0.3}Mg_{0.7}$–MOF-74 presents the largest 1-hexene adsorption capacity of 152.7 mg/g and the highest 1-hexene/n-hexane selectivity of 9.7 [see Figure 5(c)]. This high selectivity is 1.3 and 8 times higher than those of monometallic Co- or Mg-MOF-74 samples, respectively. Computational results suggest that Mg-MOF-74 has the strongest affinity to 1-hexene, 17.4 kcal/mol, while Co-MOF-74 has the second strongest adsorption energy of 16.5 kcal/mol. Interestingly, the 1-hexene–Co_xMg_{1-x}–MOF-74 interaction energies are significantly less exothermic [see Figure 5(d)]. To verify the predicted energy of interaction values, currently, we are working on corresponding n-hexane/1-hexene *vapor adsorption calorimetry* studies on Co_xMg_{1-x}–MOF-74 using a unique system developed at WSU. We expect that the near-zero binding energies and enthalpies of interactions at saturation measured by calorimetry are different for materials with different Co/Mg ratio.

B. Tuning n-hexane adsorption on ZIF-8-90 by controllable ligand hybridization – modification of the thermodynamics of adsorbate confinement

Very recently, Sun *et al.* (2019a) demonstrated that for ZIFs, linker hybridization modified both surface properties and pore dimensions (see Figure 6), which led to enhanced n-hexane adsorption. Specifically, hybriding ZIF-8 with ZIF-90 resulted in ZIF-8-90 with binary organic ligands, both 2-MeIM (linker of ZIF-8) and OHC-IM (linker of ZIF-90). Interestingly, as the OHC-IM percentage increases from 30% to 80%, the micropore size decreases from 0.7 to 0.6 nm, while the mesopore dimension increases monotonically from 2.2 to 3.3 nm. On the other hand, the framework polarity increases as more OHC-IM linkers are introduced,
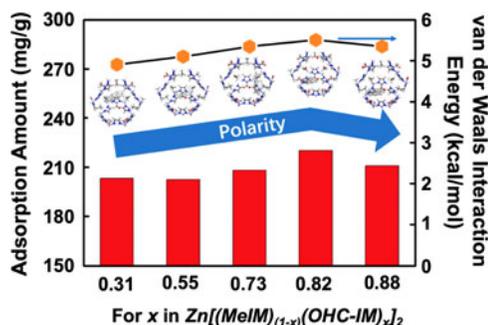

Figure 6. (Colour online) Confinement effects are modified by ligand hybridization for n-hexane adsorption on ZIF-8-90. The adsorption capacity, selectivity, and interaction energy are modified by tuning compositional factor, such as the type of organic ligand linker. Reprinted with permission from (Sun *et al.*, 2019a). Copyright 2019 American Chemical Society.

which leads to stronger *n*-hexane–ZIF-8-90 guest–host affinity. The highest *n*-hexane adsorption capacity is observed for the sample with 80% OHC-IM linker. This is in good agreement with the Grand Canonical Monte Carlo simulation results, which suggest that ZIF-8-90 with 80% OHC-IM has the strongest binding with *n*-hexane resulting in the most exothermic van der Waals interaction energy (Sun *et al.*, 2019a). A subsequent *adsorption calorimetry* study is being carried out in the WSU group.

V. CONCLUDING REMARKS

Experimental thermodynamic studies on MOFs with true polymorphism, ultrahigh porosity, and the simplest structures have been carried out. Integrating calorimetry and low-temperature heat capacity measurements with computational prediction, we have learnt that the subtle microscopic molecular and topological (structural) level variations of MOFs can be mirrored by macroscopic experimentally measured thermodynamic parameters. Realizing there is not much energetic cost to synthesize MOFs with ultrahigh surface areas or porosity, and different polymorphs, the next step is to take advantage of such properties for appropriate applications and to further study the thermodynamics – chemistry – topology – functionality relations of MOFs in a particular application, such as separation of complex mixtures.

ACKNOWLEDGEMENTS

Akimbekov, Z. and Navrotsky, A. (**2016**). "Little thermodynamic penalty for the synthesis of ultraporous metal organic frameworks," Chem. Phys. Chem. **17**, 468–470.

Akimbekov, Z., Katsenis, A. D., Nagabhushana, G. P., Ayoub, G., Arhangelskis, M., Morris, A. J., Friščić, T., and Navrotsky, A. (**2017**). "Experimental and theoretical evaluation of the stability of true MOF polymorphs explains their mechanochemical interconversions," J. Am. Chem. Soc. **139**, 7952–7957.

Arhangelskis, M., Katsenis, A. D., Novendra, N., Akimbekov, Z., Gandrath, D., Marrett, J. M., Ayoub, G., Morris, A. J., Farha, O. K., Friščić, T., and Navrotsky, A. (**2019**). "Theoretical prediction and experimental evaluation of topological landscape and thermodynamic stability of a fluorinated zeolitic imidazolate framework," Chem. Mater. **31**, 3777–3783.

Calvin, J. J., Asplund, M., Akimbekov, Z., Ayoub, G., Katsenis, A. D., Navrotsky, A., Friščić, T., and Woodfield, B. F. (**2018**). "Heat capacity and thermodynamic functions of crystalline and amorphous forms of the metal organic framework zinc 2-ethylimidazolate, Zn(EtIm)2," J. Chem. Thermodyn. **116**, 341–351.

Cook, T. R., Zheng, Y. R., and Stang, P. J. (**2013**). "Metal-organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal-organic materials," Chem. Rev. **113**, 734–777.

Furukawa, H., Cordova, K. E., O'Keeffe, M., and Yaghi, O. M. (**2013**). "The chemistry and applications of metal-organic frameworks," Science. **341**, 1230444.

Li, G., Sun, H., Xu, H., Guo, X., and Wu, D. (**2017**). "Probing the energetics of molecule-material interactions at interfaces and in nanopores," J. Phys. Chem. C. **121**, 26141–26154.

Nagabhushana, G. P., Shivaramaiah, R., and Navrotsky, A. (**2018**). "Thermochemistry of the simplest metal organic frameworks: formates [M(HCOO)2]· xH2O (M = Li, Mg, Mn, Co, Ni, and Zn)," J. Chem. Thermodyn. **118**, 325–330.

Rosen, P. F., Calvin, J. J., Dickson, M. S., Katsenis, A. D., Friščić, T., Navrotsky, A., Ross, N. L., Kolesnikov, A. I., and Woodfield, B. F. (**2019**). "Heat capacity and thermodynamic functions of crystalline forms of the metal-organic framework zinc 2-methylimidazolate, Zn (MeIm)2," J. Chem. Thermodyn. **136**, 160–169.

Sun, H., Jiang, H., Kong, R., Ren, D., Wang, D., Tan, J., Wu, D., Zhu, W., and Shen, B. (**2019a**). "Tuning n-alkane adsorption on mixed-linker ZIF-8-90 via controllable ligand hybridization: insight into the confinement from an energetics perspective." Ind. Eng. Chem. Res. **58**, 13274–13283.

Sun, H., Ren, D., Kong, R., Wang, D., Jiang, H., Tan, J., Wu, D., Chen, S., and Shen, B. (**2019b**). "Tuning 1-hexene/n-hexane adsorption on MOF-74 via constructing Co-Mg bimetallic frameworks," Microporous Mesoporous Mater. **284**, 151–160.

Wu, D. and Navrotsky, A. (**2015**). "Thermodynamics of metal-organic frameworks," J. Solid State Chem. **223**, 53–58.