Heat Capacity and Thermodynamic Functions of Loaded and Unloaded Forms of Several Zinc Imidazole Metal Organic Frameworks

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Metal organic frameworks (MOFs) may be useful in a variety of applications, mostly related to their capacity to store gases and catalyze reactions. As several MOFs are mechanically milled, they transition through different structures, progressing toward denser and more energetically stable polymorphs. In this talk, we have measured the constant pressure heat capacities of several zeolitic imidazolate frameworks (ZIFs) based on the imidazole linker exhibiting identical chemical compositions and different framework structures. Specifically, the crystalline $Zn(EtIm)_2$ frameworks of zeolite rho (RHO), analcime (ANA), and β-quartz (*qtz*) topologies were compared to each other and to the amorphous form of the material prepared by milling. We have also measured the crysalline forms of $Zn(MeIm)_2$ and its *dia* polymorph empty and loaded with CO_2. Molar heat capacities were measured from 1.8 to 300 K using a Quantum Design Physical Property Measurement System (PPMS), and the data were fit to a sum of theoretical functions below 15 K, orthogonal polynomials from 10 to 60 K, and a combination of Debye and Einstein functions above 50 K. These fits were then used to generate $C_{p,m}°$, $\Delta_0^T S_m°$, $\Delta_0^T H_m°$, and $\Phi_m°$ values at smoothed temperatures from 0 to 300 K. Though the enthalpies of transition scale with molar volume or density, the entropies of transition show more complex behavior, and the free energies of the three energetically less stable polymorphs (RHO, *am*-RHO, and ANA) are very similar. For the $Zn(MeIm)_2$ materials, there is clear evidence of CO_2 and as expected the heat capacity of the CO_2 guest molecules is quite different from that of the gas.