

Chemical Engineering Doctoral Defense

Structure, thermodynamic stability, and energetics of guest-host interactions in hybrid materials: polymer derived ceramics (PDCs) and metal organic frameworks (MOFs)

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Abstract

This thesis work systematically investigates structure-stability relations in various polymer derived ceramic (PDC) systems and metal organic frameworks (MOFs). The investigation of silicon carbides (SiCs) confirms greater thermodynamic stabilization of PDCs with increasing mixed bonding (Si bonded to both C, O and/or N). The study of more complex silicon oxycarbide (SiOC) structures, shows stabilization of SiOCs with increasing pyrolysis temperature (between 1200-1500 °C), and points to dissimilarities in the stabilizing effect of different mixed bonding environments (SiO₃C, SiO₂C₂, or SiOC₃) and their relative amounts. Investigation of quaternary silicon oxycarbonitride (SiC(N)(O)) materials suggests increased stabilization of SiOCs systems with the incorporation of N content, and superior stabilizing effect of SiN_xC_{4-x} compared to SiO_xC_{4-x} mixed bonds. Additionally, investigation of the energetics of metal filler (Nb, Hf, Ta) incorporation in SiOCs shows that choice of metal filler influences the composition, structural evolution, and thermodynamic stability in PDCs. The incorporation of Ta fillers can stabilize otherwise unstable SiO₃C mixed bonds. Independent of metal incorporation or lack thereof, in SiOCs systems, higher pyrolysis temperature (1200-1500 °C) forms more stable ceramics. Overall, in PDCs the stabilizing effect of order/disorder of the free carbon phase is system-dependent. The work on (MOFs) highlights stabilization trends obtained from the investigation of zeolitic imidazolate frameworks (ZIFs) and boron imidazolate frameworks (BIFs) based on azolate linkers. Investigation of the energetics of metal (Co(II), Cu(II), and Zn(II)) substitution in isostructural ZIFs shows that in MOFs the stabilizing effect of metal is dependent on both framework topology (diamondoid (dia) > sodalite (SOD)) and dimension (2D > 3D). Thermodynamic analyses of metal substitution (Ag(I), Cu(I), and Li(I)) in isostructural BIF systems confirm increase in density as general descriptor for increased stabilization in MOFs. The study of energetics of guest-host interactions, during CO₂ incorporation in MOFs shows strong dependence of energetics of adsorption on choice of linker and metal. Lastly, we quantitate the thermodynamic driving force for the reaction of metal organic frameworks (MOFs) with carbon dioxide, leading to a metal-organic carbonate phase. Overall, Both PDCs and MOFs show complex energetic landscapes, with identifiable system-dependent and general stabilization trends.



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