Sorption-based separation of acetylene, ethylene and ethane in a porous metal organic framework

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Separation of small hydrocarbon gases is crucial for many industrial processes but current separation techniques require significant amounts of energy. Here, we evaluate the pure and functionalized metal organic framework UiO-66(Zr) as solid adsorbent and explore its potential for separation of C_2H_2, C_2H_4 and C_2H_6. We performed calorimetry measurements at 195 K and 293 K and find that, at 195 K, C_2H_2 exhibits the highest adsorption enthalpy with a significant gap of ∼6 kJ/mol to C_2H_4 and ∼9 kJ/mol to C_2H_6, which makes sorption-based C_2H_2/C_2H_4 and C_2H_2/C_2H_6 separation possible. Using *ab initio* calculations at the density functional theory level, we can qualitatively and quantitatively explain the exact mechanisms that lead to the observed difference in binding affinity. We further improved the binding capabilities of UiO-66(Zr) by adding NO_2 functional groups, which leads to an increase in adsorption enthalpy of all three gases by 15–20% and increases the gap to ∼9 kJ/mol and ∼10 kJ/mol for C_2H_4 and C_2H_6, respectively. Our research suggests that UiO-66(Zr) has promise as a solid adsorbent in C_2H_2, C_2H_4 and C_2H_6 separation applications and that functionalization can be used to increase effectiveness and specificity.