

Cooperative Adsorption and Gas Separations in Metal–Organic Frameworks

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The tunability of metal–organic frameworks offers the possibility of designing powerful new adsorbents that selectively adsorb and release gas molecules in a cooperative manner. An initial example of such a material was realized in mmen-Mg₂(dobpdc), which exhibits step-shaped CO₂ adsorption isotherms arising from a cooperative insertion mechanism that leads to ammonium carbamate chains running along the pore surface. This mechanism has now been widely elaborated, leading to diamine-appended adsorbents that cycle at high capacity in the presence of water, and are capable of efficiently separating CO₂ from flue gas emissions, air, natural gas, and biogas. Stabilization of the materials through functionalization with appropriately structured tetraamines further enables cooperative CO₂ capture at high temperatures, as well as regeneration via steam stripping. This type of cooperative mechanism has been extended to the selective adsorption of CS₂, and a related mechanism has been shown to be operational in alcoholamine-appended frameworks. In addition, efforts to expand the scope of cooperative adsorption have led to new metal-organic frameworks containing: (i) chains of high-spin iron(II) sites that can cooperatively adsorb CO via a spin transition mechanism, (ii) chains of redox-active cobalt(II) sites that exhibit negative cooperativity upon uptake of O₂, and (iii) binuclear metal complexes that enable the cooperative adsorption of NH₃ through a ligand insertion mechanism. Finally, the first porous materials that can effectively capture gases such as CO₂ at elevated temperatures in the range 200–300 °C will be introduced.