Designing New Cooperative Adsorbents For Gas Separations

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Introduction

Chemical separations currently consume 10-15% of all energy usage.1 Generally, industrial gas separations use energy intensive distillation processes, whereas selective adsorbent-based technologies are far more efficient.2

Traditional adsorbents show a tradeoff between selectivity and regenerability. Biologically-inspired cooperative adsorption, where binding at one site promotes binding at neighboring sites, can retain selectivity while endowing very easy adsorbent regeneration, providing additional energy savings.3 Here, we demonstrate the first example of rationally designing a selective, cooperative adsorbent and establish design principles for future adsorbents.4

MOF Design and Synthesis

MOFs with open metal sites can be highly selective adsorbents.5 In theory, an adsorbate-induced response at one site can, if it influences binding at neighboring sites, can propagate down a chain to create a cooperative adsorbent (left).

MOFs containing Fe2+ sites with the proper ligand field can undergo a spin transition upon binding CO, inducing a structural rearrangement and highly selective CO adsorption.6 We synthesized Fe2Cl2(bbta), which contains highly interconnected chains of these Fe2+ sites. This allows for cooperative CO adsorption by promoting this spin transition down the chain.

Gas Adsorption Isotherms and Separation Performance

Adsorption isotherms of CO reveal a step shape, indicative of cooperative adsorption (left).

The step position moves drastically with temperature to recover of large CO quantities with very small temperature swings (comparison with other selective adsorbents, center).

The step position can be tuned by linker modification, with shifted step-shaped isotherms shown in Fe2Cl2(btdd) (right). This allows this mechanism to be used in different separation processes.

Characterization of the Spin Transition Mechanism

Characterization of the activated and CO-dosed material by X-ray diffraction, Mössbauer spectroscopy, and SQUID magnetometry show a transition from high-spin Fe2+ in the activated material to low-spin Fe2+ upon binding CO.

In situ characterization techniques show that the iron sites remain high-spin below the onset step pressure, and that once triggered, each crystallite fully converts to low-spin with no intermediate phase. This agrees with a fully cooperative spin transition mechanism.

All characterization methods and gas sorption show that the desorption is fully reversible over several cycles.

References: