

ELASTIC LAYERED METAL-ORGANIC FRAMEWORK SORBENTS FOR CARBON CAPTURE

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Introduction

Elastic layered metal-organic framework (ELM) adsorbents exhibit a flexible two-dimensional latent porous crystalline structure. ELMs undergo abrupt reversible gated sorption transitions from an empty collapsed structure to a filled expanded porous state through cooperative adsorption of guest molecules between layer planes. Gated adsorption has been observed for methane, nitrogen, carbon dioxide, and other gases [1]. The ELM gating transition and associated hysteresis loop is different than the gas condensation phase transition commonly observed for other nanoporous adsorbents, in that it is induced by rearrangement of the MOF structure rather than by adsorbent pore size distribution effects.

Certain ELMs have very high selectivity for CO₂ adsorption from gas mixtures, and are intriguing adsorbents for cost reductions in carbon capture and storage operations for CO₂ removal from nitrogen and other flue gases in post-combustion separations or from hydrogen in pre-combustion separation (e.g. following coal gasification). Moreover, ELMs have attractive sorption capacities, enthalpies, and isotherm features for efficient recovery of captured CO₂ using temperature or pressure swing adsorption [2]. Preliminary studies also indicate that ELMs have good stability in the presence of water vapor, with largely reversible recovery of CO₂ sorption capacity upon drying after exposure to steam [3]. ELMs thus merit further investigation as materials for sorbent-based capture of industrial CO₂ emissions.

In this paper, molecular simulation results are reported for ELM-11 [Cu(BF₄)₂(bpy)₂ (bpy = bipyridine)] and ELM-12 [Cu(bpy)₂(OTf)₂ (OTf = trifluoromethanesulfonate)] for their use as carbon capture adsorbents for the separation of CO₂ from pre- and post-combustion gas mixtures. Adsorption capacity, CO₂ selectivity, and isosteric heat of adsorption for pure CO₂ and binary CO₂/H₂ and CO₂/N₂ mixtures were calculated via grand canonical Monte Carlo (GCMC) simulation at temperatures (273 to 400 K), pressures, and compositions (5 to 15% CO₂) representative of power plant flue gas streams.

Results and Discussion

GCMC simulations of CO₂ capacity above the gate pressure using a rigid model of ELM-11 agree well with experimental isotherms at 273 K. The CO₂ sorption capacity (140 mg/g) and heat of adsorption on ELM-11 are competitive with

commodity adsorbents at realistic process conditions. Molecular simulations project a CO₂/N₂ selectivity exceeding 600 at 300 K (Fig. 1), a capture ratio significantly higher than common activated carbons and zeolites. The simulated CO₂ selectivity is comparable to experimental results for separating CO₂ from N₂ and O₂ by temperature swing adsorption from 268 K to 311 K using ELM-11. Desorption of captured CO₂ of more than 99% purity was obtained from a ternary mixture of 40% CO₂, 48% N₂ and 12% O₂ at 268 K [2].

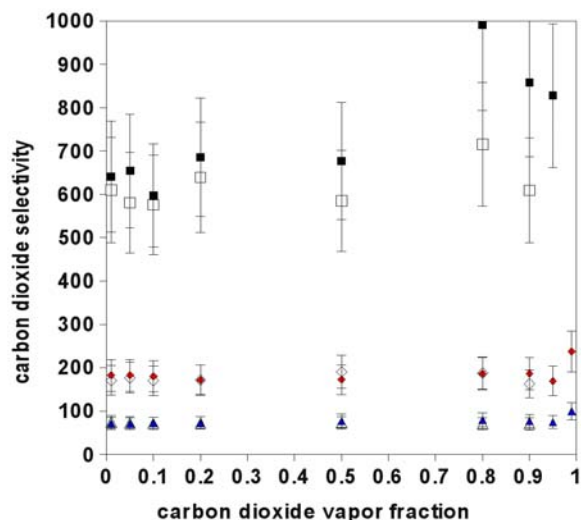


Fig. 1: Sorption selectivity for CO₂ capture on rigid open ELM-11 from binary CO₂/N₂ mixtures at 300 K (squares), 350 K (diamonds) and 400 K (triangles) and 100 kPa (filled symbols) and 200 kPa (open symbols).

GCMC simulations on ELM-11 for CO₂/H₂ mixtures representing shifted synthesis gas were also carried out and CO₂ selectivities of 1000 and 400 were obtained at 298 and 373 K respectively. These compare favorably with reported values for commercial adsorbents used for gas separations. To investigate framework flexibility effects on CO₂ sorption in ELM-11, a hybrid Monte Carlo/molecular dynamics (MCMD) method was applied. CO₂ adsorption isotherms showed good agreement with experiments at 273 K. Mixed-gas simulations yield CO₂/N₂ selectivities of 70 and 20 respectively at 300 K and 350 K, still comparable or superior to other common adsorbents but lower than the selectivity range predicted from rigid model framework simulations.

References

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