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Research Highlight

MOF adsorbents capture CO_2 on an industrial scale

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Combustion of fossil fuels in industrial settings, such as coal-fired power plants, steel-smelting furnaces, and cement kilns accounts for more than 70% of CO_2 emission. Although liquid amine scrubbing processes that are based on 30 wt% monoethanolamine aqueous solutions are feasible in capturing CO_2 on a large scale, significant drawbacks remain concerning the energy penalty for regeneration and environmental pollution upon their disposal after degradation [1]. Metal–organic frameworks (MOFs) are designable solid adsorbents with defined adsorption sites and tunable pore metrics, which lead to high adsorption selectivity and low parasitic energy for regeneration and recycling [1–6]. In general, the design of CO_2 MOF adsorbents is based on tethering of functional groups onto the framework backbone or exploration of structures that combine ultramicroporosity with hydrophobicity [7–11]. However, concerns about the stability and scalability of MOFs have posed a difficulty for their actual use in industrial applications. In a recent article published in *Science*, Lin and co-workers [12] report a highly stable and scalable MOF, termed Calgary Framework-20 (CALF-20, Fig. 1), with excellent tolerance to high humidity for durable CO_2 capture and direct steam regeneration at pilot-scale.

CALF-20 is constructed from square-grid layers of zinc(II) triazolates [13–15] pillared by chelating oxalate linkers to form a three-dimensional extended framework. With its inherent microporosity, the CO_2 uptake of CALF-20 is 4.07 mmol/g at 1.2 bar (1 bar = 10^5 Pa) and 293 K with a realized CO_2/N_2 IAST (ideal adsorbed solution theory) selectivity of 230 for a v:v = 10:90 gas mixture. CALF-20 exhibits exceptional robustness highlighted by the structure retaining its crystallinity and N_2 uptake even after one week of being exposed to 150 °C steam. CALF-20's CO_2 capture capacity was retained over 450,000 steam/hot air regeneration cycles and 6 d continuous exposure of real natural gas combustion at 50 °C. Furthermore, CALF-20 is economically feasible for pilot-scale testing as a result of the commercial availability of its organic linker and the inexpensive metal used to construct the framework, which was synthesized under non-solvothermal conditions with a high yield of ~90% using environmental friendly H_2O and CH_3OH. In collaboration with BASF, the synthesis of CALF-20 was scaled up to 300 kg/batch with a high space-time yield of 550 kg/(m^3 d), which makes it competitive to traditional zeolite materials. In collaboration with Svante Inc., a "Sorbent on a Roll" process was developed to coat CALF-20 on laminate stacked to form a filter that efficiently captured CO_2 and enhanced pressure durability and thermal conductivity. The carbon capture process has been demonstrated at a 0.1 t/d scale for over 2000 h treatment of cement kiln flue gas composition containing high humidity and wet acidity. Counter to traditional temperature swing adsorption (TSA) and vacuum swing adsorption (VSA), the direct steam regeneration employed in their report represents a concentration swing added on the TSA, which can desorb all the captured CO_2 to avoid the poor thermal conductivity of this porous material.

Competitive adsorption of CO_2 over H_2O is crucial for direct flue gas capture [16–19]. The kinetic CO_2/H_2O adsorption selectivity of MOFs for 15% CO_2 in the presence of up to 95% relative humidity (RH) has been determined by gravimetric adsorption and breakthrough experiments [19]. Interestingly, CALF-20 showed good affinity to CO_2 and exhibited poor water uptake within the range of $P/P_0 \leq 0.3$. Beyond our expectations, grand canonical Monte Carlo (GCMC) simulations and density functional theory (DFT) calculations revealed the CO_2 binding energy to be ca. −36.5 kJ/mol with the primary binding site being located at the middle of pores. The CO_2-MOF interaction was dominated by attractive dispersion interactions in CALF-20, which is very different from the benchmark materials, such as SIFSIX-3-Zn that possess a stronger adsorption affinity (ca. −45 kJ/mol) dominated by electrostatics interactions. On the other hand, H_2O interacts weakly with the framework of CALF-20 with binding energies as low as −17.5 kJ/mol lacking "seeds" for the formation of a hydrogen-bonded H_2O network [20]. Given the low H_2O-affinity coupled with the CO_2-philic behavior, the competitive CO_2 breakthrough of the CALF-20-polysulfone composite achieved a similar retention time under a RH <40%. Furthermore, the H_2O breakthrough was facilitated by CO_2 indicating CO_2 uptake may suppress the H_2O adsorption. These results shed light on the design of CO_2 adsorbents for direct flue gas capture; specifically, a pore structure non-ideal for H_2O is more important than a pore structure ideal for CO_2.

Overall, the industrialization of MOF materials for such a pilot-scale carbon capture application represents an appealing story across the "Death Valley of Innovation". In comparison to fundamental research, the large-scale testing requires comprehensive considerations (i.e., sorbent stability, affordability, commercial maturity) and considerably more efforts and resources to deal with all of the problems encountered on the way to practical application (i.e., large-scale synthesis, shaping and structuring, process engineering, cycling performance test). The success of CALF-20 has

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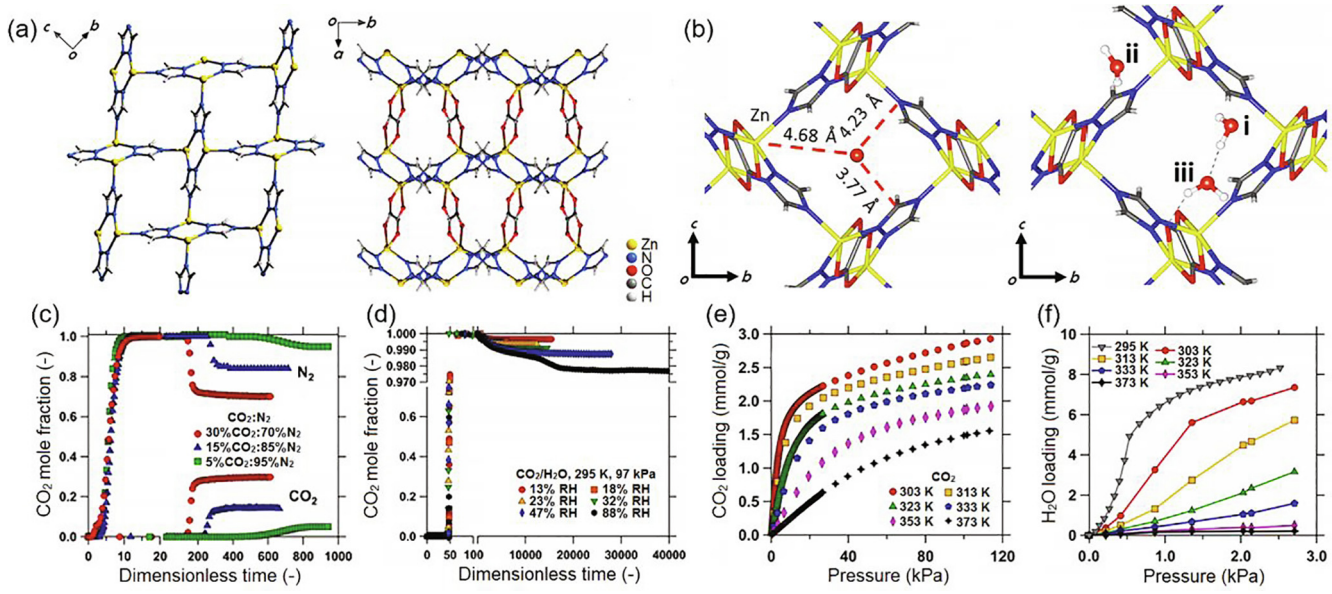


Fig. 1. (a) Projection views of the grid zinc triazolate layer and the side view pillaring of the layers by oxalate linkers. (b) Calculated CO_2 and H_2O adsorption sites. (c) Breakthrough curves for binary CO_2/N_2 gas mixtures in different ratios. (d) Competitive CO_2 breakthrough curves under different relative humidity. (e) CO_2 adsorption isotherms at 303–373 K. (f) H_2O adsorption isotherms at 295–373 K [12]. Copyright 2021, American Association for the Advancement of Science.

de-risked the implementation of MOF materials for large-scale gas separation in industrial settings, thereby paving the way to other applications on even larger scales. In the context of carbon neutrality, efficient carbon capture is one of the steps in reducing greenhouse gases, and the carbon footprint of material production and energy efficiency for capturing CO_2 and subsequent regeneration of the adsorption bed should be considered. It is worth noting that CALF-20 is not the best CO_2 adsorbent by any measure, but it is a material that fulfills all the criteria for carbon capture. More efforts are required to screen materials considering stability, affordability, scalability, and durability when applied to practical conditions.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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