Metal–organic framework for high-temperature CO_2 capture

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Carbon dioxide (CO_2) capture is a critical technology for mitigating climate change by reducing greenhouse gas emissions from industrial processes and power plants.[1,2] Among various approaches, post-combustion CO_2 capture using aqueous amines is the most established technique, providing reversible binding of CO_2 and yielding a purified CO_2 stream for subsequent sequestration.[3] However, amine-based CO_2 capture incurs relatively high energy demands for solvent regeneration and raises concerns related to corrosivity, volatility, and toxicity.[4] Additionally, the relatively low operating temperature (≤60 °C) necessitates extra cooling of industrial exhaust streams (typically >200 °C), increasing overall costs. High-temperature CO_2 adsorption offers a potential cost-effective alternative. Alkali and alkaline earth metal oxides have been explored for this purpose because they react with CO_2 at medium to high temperatures (>200 °C) to form metal carbonates.[5] Unfortunately, their performance tends to decline over repeated cycles due to volume changes, leading to particle sintering and deactivation.

Metal–organic frameworks (MOFs) have emerged as promising alternatives because of their robust, intrinsically porous structures, which support rapid CO_2 adsorption without significant structural degradation.[6] In particular, MOFs functionalized with polyamines have demonstrated exceptional CO_2 capture capabilities at moderate temperatures (~150 °C).[7] Nonetheless, extending their performance to higher temperatures remains a pressing challenge.

Metal hydrides, especially transition-metal hydride complexes, have long been known to react with CO_2 to form metal formates. Early studies established their efficiency as CO_2 reduction catalysts.[8] Building on this knowledge, a research team led by Jeffrey R. Long at the University of California recently reported a MOF-based adsorbent containing open zinc hydride (Zn–H) sites (Figure 1a).[9] This material, termed ZnH–MFU-4l, enables high-temperature post-combustion CO_2 capture with exceptional capacity, selectivity, and stability, making it suitable for direct capture from high-temperature exhaust streams.

The ZnH–MFU-4l framework is synthesized from ZnCl–MFU-4l via a formate exchange to produce $Zn(O_2CH)$–MFU-4l, followed by thermolysis at 300 °C to remove CO_2. Isothermal CO_2 adsorption measurements over a wide temperature range (25 °C to 300 °C) revealed a dramatic increase in CO_2 uptake with temperature. At 200 °C and 1 bar, ZnH–MFU-4l achieves an adsorption capacity of 3.52 mmol g^{-1}, far surpassing comparable MOFs and metal oxides. Even under low CO_2 partial pressures, the material exhibits robust adsorption due to its high adsorption enthalpy (−93 kJ mol^{-1}), which supports strong chemisorption.

The remarkable adsorption performance relies on the Zn–H sites within the MOF. Above 200 °C, CO_2 adsorbs via insertion into the Zn–H bonds to form zinc-formate (Zn–O_2CH) species. Desorption is accomplished under either pure nitrogen or vacuum, regenerating the Zn–H sites without compromising the MOF's structure or performance (Figure 1b). Under simulated steel production flue gas conditions (200 mbar CO_2 for adsorption, 20 mbar CO_2 for regeneration), ZnH–MFU-4l reached a high capacity of 3.05 mmol g^{-1} and showed exceptional long-term stability, retaining over 96% of its initial capacity after 508 cycles (150 hours). The material also remains highly selective in the presence of water and SO_2. After ten humidity-inclusive TGA cycling tests, it still retained 83% of its CO_2 capacity, compared to 95% under dry conditions.

Kinetic studies further illustrate ZnH–MFU-4l's efficiency. At 300 °C, the adsorbent reaches 90% of its equilibrium capacity within just nine seconds under a 20% CO_2 atmosphere, underscoring the favorable energetics of CO_2 insertion into the Zn–H bonds. Eyring analysis and density functional theory (DFT) calculations indicate that the Gibbs activation energy for CO_2 insertion decreases significantly with increasing temperature, explaining the material's high performance under demanding high-temperature conditions.

In summary, ZnH–MFU-4l represents a groundbreaking strategy for high-temperature CO_2 capture in industrial settings. Its unprecedented capacity, selectivity, and durability underscore the potential of MOF-based adsorbents to address pressing challenges in CO_2 capture. Given the global importance of effective CO_2 mitigation, these findings pave the way for further advances in MOF design and optimization, expanding the possibilities for next-generation CO_2 capture technologies.

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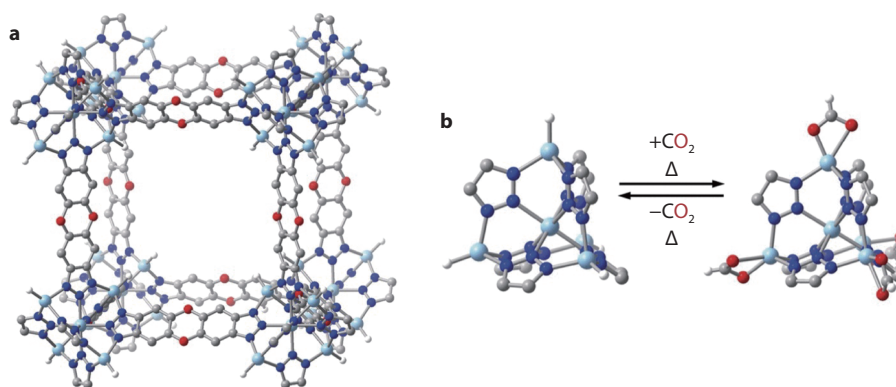
Fig. 1 **a** Structural illustration of a segment of the ZnH–MFU-4l framework. **b** (Left) Expanded view of the pentanuclear Zn cluster node. (Right) The Zn–formate species. Light-blue, gray, blue, red, and white spheres represent Zn, C, N, O, and H atoms, respectively.[9] Copyright 2024, Science.

■ CONFLICT OF INTEREST

The authors declare no competing interest.

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