Porous Materials and CO_2 capture

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Significance and Relevance

The increase in CO_2 emissions has stimulated scientific and technological developments to capture, convert, store, and remove CO_2 from the environment. We propose porous materials able to capture and separate CO_2 from N_2 by exploiting the active sites of the framework, which can host specifically CO_2 molecules. The intermolecular interactions of about 35 kJ/mol are a very good balance for favorable CO_2 capture and release. Breakthrough experiments demonstrate the efficient CO_2 separation starting from CO_2/N_2 mixtures at room temperature.

Introduction and Motivations

CO_2 capture from industry or directly from the atmosphere is a topic of extreme importance on a global scale because of the drastic climate changes, threating our ecosystem.[1] CO_2 capture technology relied on liquid amine scrubbing but due to its high energy consumption and corrosive property, CO_2 capture using solid materials has recently come a valid alternative way. The manufacture of porous materials is one of the major challenges and their permanent and tunable porosity brought them into the active research area of carbon capture and utilization (CCU) by physisorption processes which require low energy costs for gas uptake and release. This goal can be achieved through various strategies that promote the formation of metal–organic frameworks (MOFs) and porous organic frameworks or polymers (POFs or POPs).[2,3] They are diversified by their tendency to form stable structures and their degree of crystalline periodicity.

MOFs are constructed by the self-assembly of organic ligands coordinated to metal ions or metal clusters generating structures with permanent porosity, high specific surface areas and tunable topologies. Within the family of MOFs the presence of a second linker enabled to further tailor the structures generating the so-called pillar-layered MOFs. Pillars in MOFs are composed by two distinct organic ligands, one ligand is coordinated to metal nodes forming two-dimensional sheets, whilst the other one, called pillar, coordinates with the metal ions of two different planes, creating a layered and flexible structure that is suitable for CO_2 capture.

POFs boast some prerogatives derived from the stability of their 3D network of covalent bonds. These prerogatives include high thermal robustness, resistance to solvents, especially water, and remarkable volumetric and gravimetric pore capacities. Further important properties are enabled by the post-synthetic insertion of organic functional groups, each promoting specific interactions with target gas.

Results and Discussion

We fabricated a new class of POFs based on calixarene-moieties which showed outstanding adsorption properties towards CO_2, while selectively excluding N_2.[4] Such architectures enabled to incorporate macrocycle cone-like moieties with preorganized cavities and form functional porous materials containing two hierarchical levels of porosity, due to both the macrocycle shape and the framework pore architecture. These smart architectures endowed with hierarchical porosity from micro- to meso-porosity showed notable sponge-like swellability by CO_2, which was captured effectively at room temperature, even in competition with N_2, yielding CO_2 removal in column breakthrough experiments (Figure 1). POFs offer the opportunity to incorporate photoswitchable molecules into solid-state materials promising for the fabrication of responsive materials, the properties of which can be controlled on-demand.[5] A responsive porous switchable framework was synthesized by incorporating a bistable chiroptical overcrowded alkene moiety into the backbone of a rigid aromatic framework. As a consequence of the high intrinsic porosity, the resulting framework readily responds to a light stimulus, as demonstrated by solid-state Raman and reflectance spectroscopies. Solid-state ^{13}C NMR spectroscopy highlighted an efficient and quantitative bulk photoisomerization of the incorporated light-responsive overcrowded olefins in the solid material. Taking advantage of the quantitative photoisomerization, the porosity of the framework and the consequent CO_2 adsorption/desorption could be reversibly modulated in response to light and heat.

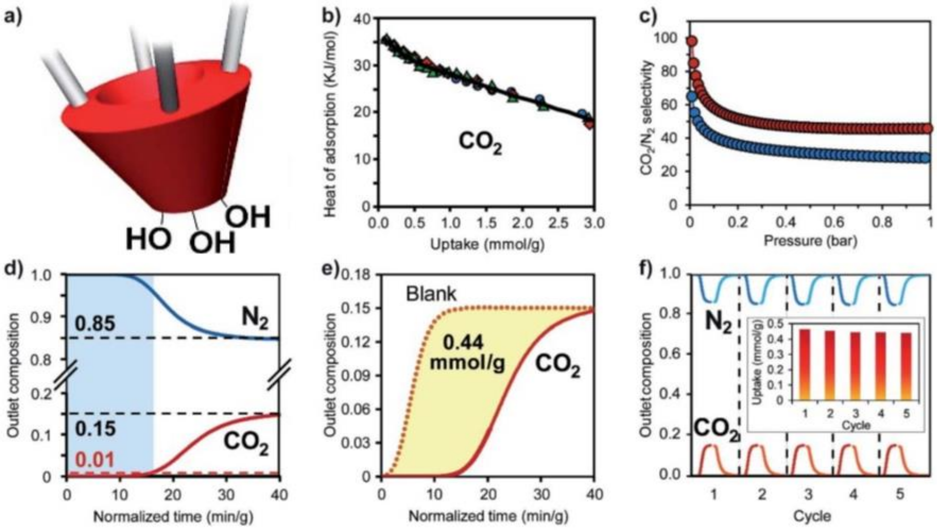

Figure 1 (a) Schematic representation of a calixarene-based POP. (b) Heat of adsorption from a microcalorimeter coupled with adsorption apparatus. (c) CO_2 over N_2 selectivity at 273 K calculated applying IAST theory to a 15 : 85 CO_2/ N_2 mixture. (d) CO_2/N_2 (15/85) breakthrough curves measured with a total flow rate of 4 sccm. (e) CO_2 breakthrough curves: the yellow shaded area was integrated to calculate the total amount of CO_2 adsorbed under dynamic conditions (f) Breakthrough experiments repeated for five cycles. The desorption was carried out by N_2 flow at room temperature. Column efficiency is constant over all cycles.

We propose a category of pillared MOFs consisting of two-dimensional layers of Me^{2+} ions coordinated with the heterocyclic anions and pillars composed of molecules bearing two carboxylate groups as new porous materials for CO_2 capture. The porous materials were characterized by a combined approach that include powder X-ray diffraction for the study of crystalline materials, FT-IR spectroscopy for the identification of functional groups, solid state NMR spectroscopy for the determination of purity and degree of crystallinity of the samples, scanning electron microscopy for the study of morphology. In situ X-ray diffraction experiments using synchrotron source light on the porous material as well as at varying CO_2 pressures, enabled to evaluate structural changes throughout the adsorption process. The MOFs exhibited high selectivity towards CO_2 with respect to N_2 (> 100) even at room temperature, and thus are promising materials for CO_2 capture from flue gas. Notably, such materials can be directly integrated into an electrocatalytic device for the conversion of CO_2 into e-fuels by using renewable energy and water.

References

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