Carbon capture: Screening for selectivity

Metal-organic frameworks (MOFs) are promising adsorbents for CO₂ capture from flue gas, but many perform poorly when exposed to flue gas containing water. Now, a computational screening approach identifies MOFs with preserved CO₂/N₂ selectivities in wet flue gas and experiments confirm their outstanding CO₂ capture performance.

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One of today's biggest challenges is to limit the increase of CO₂ in the atmosphere. Carbon capture and storage offers a potential route to help with this¹. To that end, a large number of porous adsorbents have been developed to effectively capture CO₂ from flue gas emitted by anthropogenic sources². One class of adsorbents that have great potential in CO₂ capture are metal-organic frameworks (MOFs): crystalline materials composed of metal ions connected by organic linkers^{3,4}. However, a limitation of MOFs for CO₂/N₂ separation is that they do not perform well when they are exposed to wet flue gas mixtures, as would be typical in real applications. This is because water competes with CO₂ for the same adsorption sites of MOFs and causes a significant reduction in their CO₂ selectivity. Drying the flue gas before using MOFs is thought to make the process prohibitively expensive. Therefore, design and development of MOFs that can efficiently capture CO₂ from wet flue gas has been a long-standing goal. Writing in *Nature*, Tom Woo, Susana Garcia, Kyriakos Stylianou, Berend Smit and co-workers across Europe and North America now report large-scale computational screening of materials, combined with experiments, for the data-driven design and synthesis of MOFs with high CO₂ capture performance from wet flue gas⁵.

Perhaps the most important advantage of MOFs over traditional porous materials is that their pore sizes and shapes, as well as the affinity of the pores towards different gases, can be tuned by changing the combination of linkers and metals. A diverse set of MOFs have been synthesized to date and a theoretically unlimited number of MOFs can be created. The existence of thousands of MOFs having different physical and chemical features offers an excellent opportunity to achieve high performance CO₂ separation.

At the same time, this large materials space imposes a challenge for the materials search, as it is not possible to test CO₂ separation performances of all available MOFs using purely experimental techniques. Therefore, computational screening methods play a critical role in examining a large number of MOFs in a time-effective manner to identify the most promising materials for target gas separations⁶. Experimental efforts can then be focused on those candidates.

In their work, Woo, Garcia, Stylianou, Smit and co-workers first generated a library of 325,000 hypothetical (computer-generated) MOFs. Using molecular simulations, they predicted CO₂/N₂ selectivity and CO₂ working capacity of all materials at conditions that mimic post-combustion flue gas separation processes. From these calculations, 8,325 MOFs were identified as top-ranked materials exceeding the performance of commercial zeolite 13X under dry flue gas separation conditions (CO₂ working capacity > 2 mmol/g and CO₂/N₂ selectivity > 50).

The researchers introduce the term 'adsorbaphore' to describe the common pore shape and chemistry of a binding site in the MOF that provides optimal interactions to preferentially bind to CO₂. This is inspired by the rational design of drug molecules where pharmacophores describing common features of binding sites for particular molecules are identified. CO₂ binding sites of the top-ranked MOFs were identified and categorized into three different classes of adsorbaphores. MOFs having the parallel aromatic rings adsorbaphore for CO₂ (termed A1 as shown in Figure 1) were calculated to have a low affinity for H₂O.

Next, the researchers undertook reverse-searching for the A1 adsorbaphore in the MOF database. Molecular simulations on a subclass of MOFs that contain this preferred adsorbaphore showed that predicted materials maintain an excellent CO₂ selectivity at low pressures. Moreover, selectivities of many MOFs were not affected by the presence of H₂O at flue gas conditions.

Based on these computational predictions, the researchers synthesized two MOFs (Al-PMOF and Al-PyrMOF) and demonstrated that experimentally-measured CO₂ and N₂ adsorption isotherms of these materials are in good agreement with the simulated ones. Breakthrough experiments showed that the CO₂ capture capacity of Al-PMOF is minimally influenced by humidity while an improvement of the performance was reported for Al-PyrMOF. Excitingly, the CO₂ working capacity of Al-PMOF under humid conditions outperforms that of zeolite 13X and activated carbon. This finding smartly demonstrates the data-driven design of a new MOF material with extraordinarily high CO₂ capture potential from wet flue gas.

The most exciting aspect of this study is linking computational screening and synthesis of the corresponding materials through the identification of structural motifs called adsorbaphores, which enhances the synthetic viability of the approach. This work offers a foundation for future studies to identify adsorbaphores in MOFs that provide optimal interactions to preferentially bind different guests such as CH₄ and H₂, which can eventually accelerate the design of MOFs for numerous gas storage applications. Extending the results of this work to various gas separation processes could also be fruitful in the discovery of targeted adsorbent materials. For example, MOFs examined in this study may also have the potential to capture CO₂ from natural gas mixtures. Natural gas in reservoirs contains CO₂ and H₂O, which reduce the energy content of natural gas and cause corrosion in pipelines.

Finally, it would be interesting to test the MOFs synthesized in this study under industrial operating conditions to accurately assess their real-world performance and stability. The future holds great promise for the large-scale applications of MOFs but further technical and economical evaluation of the full CO₂ capture process using the new MOFs will be crucial in order to lead to a new MOF-based CO₂ separation technology.

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Figure 1. Structural representation of the two MOFs identified for CO₂ capture from wet flue gas mixtures. Panel **a** shows Al-PMOF and panel **b** shows Al-PyrMOF. Adsorbaphore A1 which represents the planar aromatic systems where CO₂ binds in between is shown by a red box. Atom color code: pink: Al; grey: C; blue: N; red: O and pale yellow: H. Images are reproduced from ref.⁵, Springer Nature Limited.

References:

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