

Application of metal-organic frameworks for CO₂ capture

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Abstract. The emission of carbon dioxide (CO₂) is gradually increasing, and CO₂ adsorption from post-combustion processes in thermal power plants could be a viable option. As a solid adsorbent for CO₂ capture, metal-organic frameworks (MOFs) have higher selectivity and capacity for flue gas. Compared with traditional adsorbents, calgary framework 20 (CALF-20) that belongs to a zinc-based MOFs, efficiently captures CO₂ from flue gas and is affordable and durable also, which lays the foundation for its large-scale production. This article will introduce the overall idea of CO₂ adsorption, the structure of CALF-20, selectivity for N₂ and H₂O, competitive adsorption with H₂O-CO₂ and durability, and verify the excellent performance of CALF-20 with experimental results. In addition, the possibility of mass production was also shown. Specifically, CALF-20 is not as difficult to large scaling produce as other MOFs. In fact, its large-scale industrial production is feasible with its advantages of low cost, high yield, stability, environmentally friendly and safety.

Keywords: CO₂ capture, metal-organic frameworks, CALF-20, selectivity, large-scaling.

1. Introduction

The man-made carbon dioxide (CO₂) emissions sources lead to a serious environmental problems-global warming. In the past decades, the global population increased in an exponential way, from less than two billion people in 1850 to eight billion in 2020. With the increase of population and development of the industries, the energy demand is growing rapidly, and almost all of energy is from fossil fuels. As a result, the CO₂ emissions are rising and more than 35 billion tons CO₂ were emitted in 2020 [1], where the main CO₂ sources are almost coal, oil and natural gas combustion. If the emissions continue to increase in an exponential way, our environment will be badly hurt and the earth might will no longer be fit for human living. How to effectively reduce CO₂ emissions has become increasingly important.

Three main ways in carbon capture processes can be realized [2], including post-combustion CO₂ capture, pre-combustion CO₂ capture and oxy-combustion CO₂ capture. For post-combustion CO₂ capture, CO₂ components are separated from complex fuel flue gases and stored and would drastically cut yearly emissions worldwide. The typical coal-fired power plant's post-combustion flue gas composition includes N₂, CO₂, H₂O, O₂, SO₂, SO₃, NO_x, HCl, CO, Hydrocarbons and Hg [2]. The main post-combustion flue gases are N₂, CO₂, H₂O and O₂, especially N₂ and H₂O cannot be ignored either. In addition, the steam from the flue gases might make the materials unstable and O₂ will oxidize the reactive groups which could make materials ineffective and shorten the service lifetime. Therefore, the materials are supposed to be stable in a steam environment and have the properties of high CO₂/N₂ selectivity and high CO₂/H₂O selectivity. In summary, the materials worked in the power plan is supposed to have the properties of high CO₂/N₂ selectivity, high CO₂/H₂O selectivity, high capacity and durability.

The main current CO₂ capture materials are aqueous alkanolamine absorbents, solid porous adsorbent materials. For CO₂ capture, productivity, and purity, adsorbents must show some special properties such as high CO₂ capacity and poor N₂ affinity [3]. The aqueous ammonia, one of the aqueous alkanolamine absorbents, are widely utilized for CO₂ absorption because of its high capacity and low energy consumption. Due to the reversible reaction in the adsorption process, ammonia cannot be fully absorbed, and the escaped ammonia can result in environmental pollution and even cause potential safety problems [4].

The activated carbon is widely used because it cost little and it's easy to buy from the manufacturers. However, the activated carbon has lower capacity compared to zeolites. At low pressure, a typical

adsorbent, zeolite-13X, has high CO₂ capacity. However, it has a great affinity for water, which causes it to lose CO₂ performance in moist environments [5]. Metal-organic frameworks (MOFs) show much higher adsorption capacity and high selectivity, thus making them ideal adsorbents for carbon capture. These types of MOFs materials have been widely used in various fields, such as environmental pollutant removal, energy battery design and development, and disease analysis and treatment. Therefore, finding organometallic frameworks with lower cost, simpler raw materials and commercialization is the goal. With these advantages, this material can be large-scaling to reduce carbon in the atmosphere. MOFs represent a novel type of crystalline porous solid materials constructed by orderly splicing organic connectors between metal nodes. Some MOFs are highly valued as solid sorbents to capture CO₂ due to its high selectivity, high capacity, durability, low cost and so on. For this reason, this research will discuss the application performance of different MOFs-based functional materials in CO₂ adsorption.

2. Application of MOFs for CO₂ adsorption

Calgary framework 20 (CALF-20), one of the MOFs, is distinguished from other unstable and undurable MOFs. The raw materials are commercially available in a low price and the solvents to synthesize can be water and methanol mixed solvents. The requirements to capture CO₂ are showed above, but most current MOFs cannot reach the goal because they are not stable or durable. In addition, the cost and scalability of synthesis can be considerable too. Most MOFs contain costly, noncommercial-grade organic linkers or require aprotic solvents, such as diethyl or dimethyl formamide. While the CALF-20 just need some commercially raw materials as raw materials and the solvents to synthesize can be water and methanol mixed solvents.

2.1. Structure

Zinc-triazole-oxalate-based CALF-20 shows excellently selective physisorption for CO₂, which makes it appealing for possible CO₂ capture applications. As shown in Fig. 1, 3-dimensional (3D) pore structure and 3-dimensional (3D) lattice are formed by layers of 1,2,4-triazolate-bridged zinc(II) ions supported by oxalate ions in CALF-20 [6].

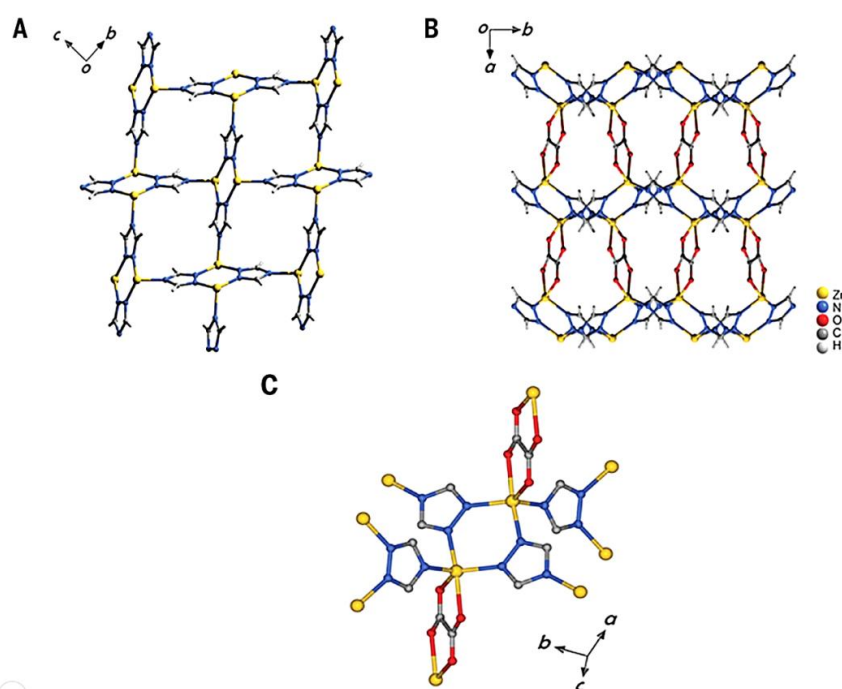


Fig. 1 CALF-20 single-crystal structure [6]. (A) The grid of zinc triazolate in two dimensions. (B) An orthogonal view of (A) explained the columnar structure of oxalate anion in zinc trinitride layer. (C) An image of the coordination sphere of zinc with the H atoms removed.

The physisorption of CO₂ is reinforced by summation of interaction which refers to the improved van der Waals interactions within the pores resulting a stronger dipole moment and a higher affinity to CO₂ [6]. The resulting interaction is stronger than hydrogen bonding which is responsible for water adsorption. Thus, there does not exist functional groups for water to bond at a low relative humidity. The zero-loading heat of CO₂ is −33.5 kJ/mol in multicomponent CO₂/N₂/H₂O simulation which is higher in absolute value than that of water with value of −17.5 kJ/mol [6]. Zero-loading heat refers to the heat of a negligible amount of gas (zero-loading) is adsorbed onto a surface. This result convinces that CALF-20 has a better affinity towards CO₂ water at a very low partial pressure.

2.2. CO₂/N₂ selectivity

CALF-20 has performance of high CO₂/N₂ selectivity. Detail information will be presented including the typical approach of calculation and simulation. The volumetric and gravimetric methods can be used to determine the isotherms of CO₂ and N₂ at different temperatures of a single component [7]. Single-component breakthrough studies with CO₂ and N₂ were carried out at 0.97 bar and 22 °C. Helium can be served as the carrier gas in these studies. The balanced helium breakthrough N₂ single-component tests at 15%, 50%, and 100% mole fraction are shown in Fig. 2. In this instance, temperature histories and breakthrough curves agreed with simulations and observations. Temperatures were projected by simulations to peak and then decline following the adsorptive heat front [7].

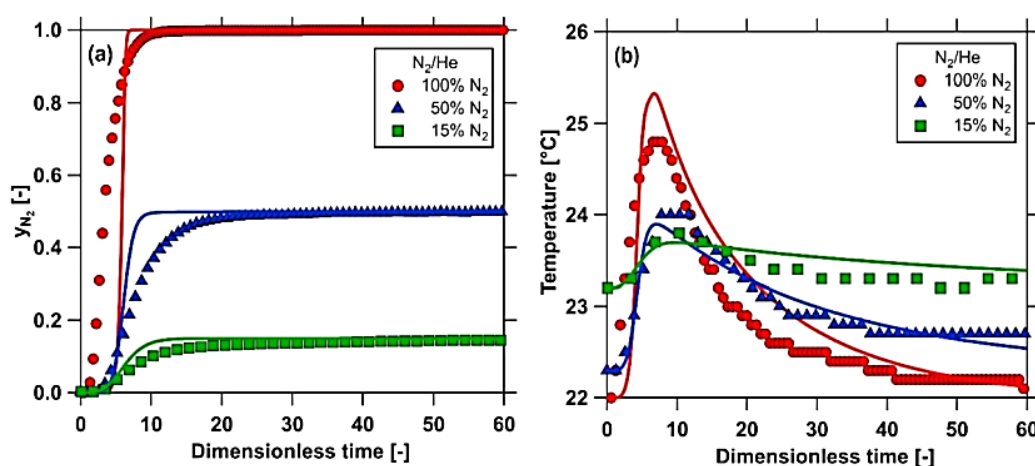


Fig. 2 Analysis of single component N₂ at various experimental conditions [7]. (a) N₂ breaking point curves; (b) Temperature history for N₂.

The competitive CO₂/N₂ loadings are explained with an enhanced dual-site Langmuir model. Using the EES technique, 5/95 CO₂/N₂ competitive breakthrough was predicted and the competitive CO₂/N₂ DCB was simulated [7]. Using the EES technique, competitive CO₂/N₂ loadings were computed from adsorption breakthrough curves. Every site has a N₂ saturation capacity that is equivalent to the matching CO₂ saturation capacity point [8].

2.3. CO₂/H₂O selectivity

H₂O exists in the process of adsorption of CO₂ in post-combustion, the performance of the material is demanding. Specific influence principals and test results are presented. Water vapor included in the acidic gas in post-combustion process in thermal power plants poses a major challenge to the application of MOFs in carbon capture, as it competes with CO₂ for adsorption and affects the stability, durability and durability of the material. H₂O can affect the MOFs sorption performance through various mechanisms, including competitive adsorption, hydrolysis, and pore blockage. First, because of the competitive connection between water and CO₂ at the active binding sites, the MOFs family's CO₂ collection capacities are reduced in humid circumstances. The adsorption capacity of MOFs for the target gas may be reduced as a result of the stronger adsorption of water on its surface, which may

impede the adsorption of carbon dioxide. Second, because water has a stronger affinity for metal ions than other substances, some water-soluble MOFs adsorbents that many metals utilized in, water causes their hydrolysis and causes structural damage to the network. Furthermore, water molecules tend to obstruct the pores of the MOFs, thereby reducing its porosity and surface area. This obstruction limits the accessibility of CO₂ molecules to active sites within the material, leading to a decrease in its capacity for CO₂ adsorption.

For zeolite 13X, it is evident that CO₂ emerges and attains during a dimensionless time, $t=100$, an outlet composition of 1, in every dry and humid scenario. Using CO₂ as the CALF-20 carrier gas (Fig. 3a), breakthroughs in both dry and humid conditions were compared. Around $t \approx 50$ in cases that are dry and humid, CO₂ breaks through here. Furthermore, in stark contrast to zeolite 13X, CALF-20 maintains CO₂ capacity for competitive CO₂-H₂O loadings up to 40% RH until the loading eventually drops at very high RH values (Fig. 3b). In Fig. 3c, the loading of both pure H₂O and H₂O increase with increasing relative humidity, while the loading of CO₂ decreases continuously. The H₂O breakthrough curves for the air and CO₂ carrier gas scenarios are also compared at similar relative humidity values. The zeolite 13X case shows that water adsorption is not impacted by CO₂ because the waterfronts in these two cases break almost simultaneously.

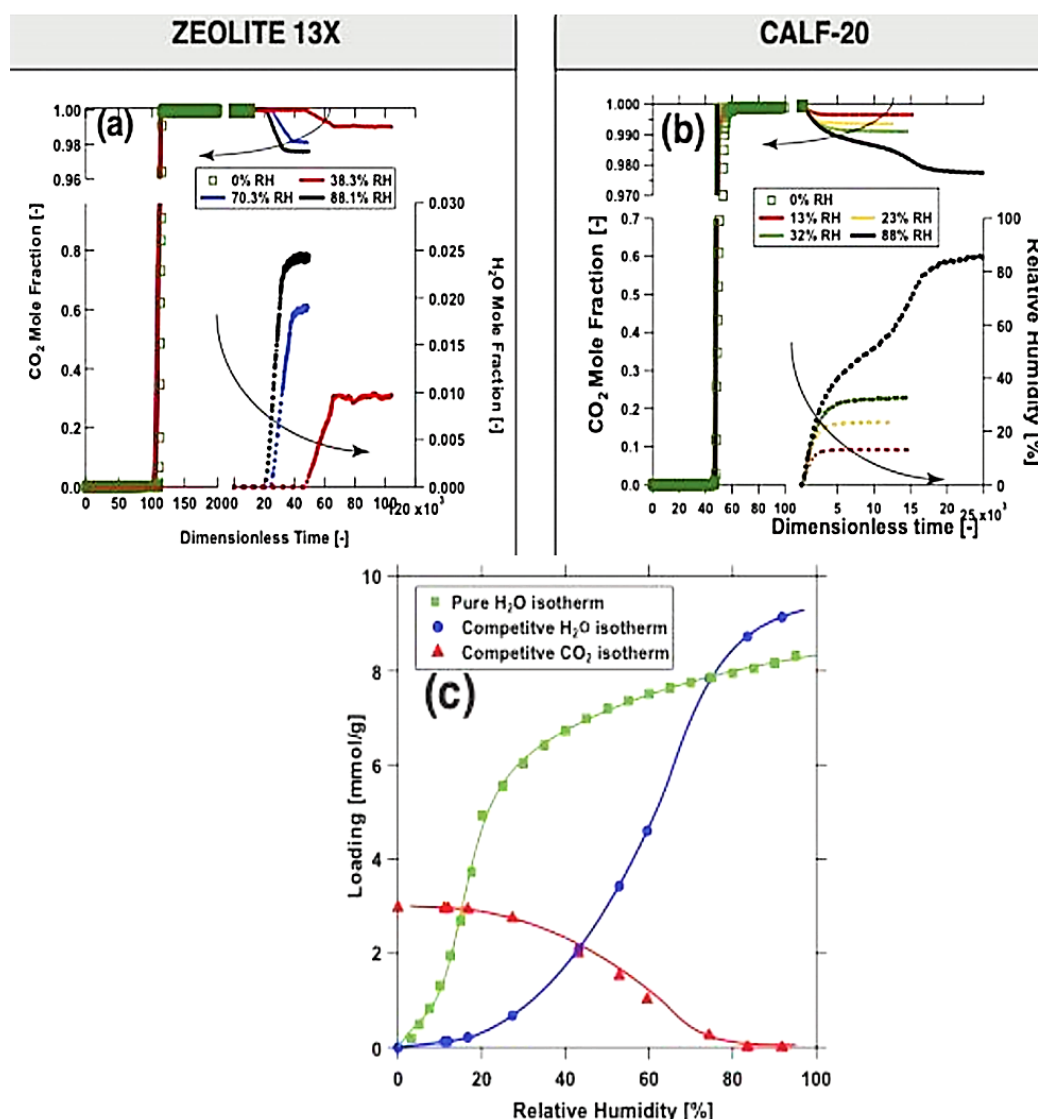


Fig. 3 Zeolite-13X and CALF-20 competitive loadings and a summary of ground-breaking experiments [9]. The CO₂ breakthrough curves of zeolite 13X (a) and CALF-20 (b) for circumstances that are both dry (symbols) and humid (lines). (c) The competitive isotherm of pure H₂O, H₂O, CO₂.

3. Scaling possibility

In the industrial setting, materials must withstand stresses during regeneration through variety swing process and absorb CO₂ from flue gases from post-combustion processes that contain acid gasses and water vapor at 100 °C. This puts a lot of pressure on the material's durability. Most modern MOFs are unable to withstand even normal moisture levels, steam, or other. However, the CALF-20 is robust enough to withstand these advancements. It has demonstrated good stability, making it have great potential in large-scale applications.

The high cost of different MOFs syntheses is one of the limits for large-scale applications. Most MOFs contain costly, noncommercial-grade organic linkers or require aprotic solvents, such as diethyl or dimethyl formamide. Certain linkers, and less frequently the metal itself, are frequently too expensive. Furthermore, the economics of synthetic process conditions might have a significant impact. High-pressure equipment, for example, not only leads to high costs but also poses significant safety hazards during use.

But as CALF-20, the commercially components are in large quantities at a low cost such as oxalic acid and triazoles. The solvents employed in the synthesis process include methanol and water of the CALF-20 which are commercially available too. The reaction solvent is a water and methanol mixture solvent, which represents <25 wt% with ongoing improvements. Therefore, it also led a safety and environmental way to synthesis the CALF-20. For CALF-20, it is possible to get an exceptionally high solid content of >35% (total dried MOFs divided by total solvents utilized). With a yield of over 90%, the reaction time is acceptable, and the proportion of solid content in total is high, the precipitation stage has an excellent space-time yield (STY) of 550 kg/m³day while Zeolites have STYs of between 50 and 150 kg/m³day [10]. In summary, CALF-20 can be large-scale applied due to its advantages of low cost, commercially available raw materials, high yield and steam stability.

4. Conclusion

This research analyzed the specific application performance of MOFs based functional materials in CO₂ capture. CALF-20 is one of MOFs that based on zinc-triazole-oxalate for applications in CO₂ capture. Compared with other adsorbents, CALF-20 can be regarded as an ideal adsorption material because of has great selectivity for CO₂/N₂, high CO₂/H₂O selectivity, high stable capacity and durability. The gravimetric and volumetric approaches to determine the isotherms of CO₂ and N₂ at different temperatures of a single component and binary dynamic column breakthrough. The results show a high CO₂/N₂ selectivity, durability, steam stability and stable capacity. What's more, compared with other MOFs, the advantages of low cost, simple raw materials, simple reactive solvent, high yield and steam stability make CALF-20 has the possibility to large-scaling produce in the future. The water and methanol as reactive solvent makes the process of CALF-20 synthesis safer and more environmental. Commercially available raw materials mean lower cost. High STY of 550 kg/m³day means that CALF-20 can effectively capture CO₂. It is precisely based on the excellent application performance of this porous material in CO₂ capture that it can provide a new construction approach for the design and synthesis of CO₂ selective separation for other porous functional materials.

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