



Programming Framework Materials for Ammonia Capture

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The surface of pores in covalent organic networks was chemically modified for better ammonia capture.

Ammonia serves as an essential feedstock in several large industries, including fertilizer and explosives manufacturing, and as a key coolant in large-scale applications such as ice rinks, making it one of the most important industrial gases.¹ It is also extremely corrosive and toxic, which makes its adsorption in applications such as air remediation, gas masks, and adsorption heat pumps very challenging. The current commercial adsorbent, activated carbon, suffers from low affinity for ammonia and relatively low capacity of only 11 mmol g⁻¹.² Although recent developments in porous materials including metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have produced remarkable advances in the state-of-the-art sorbents for a variety of gases and even water vapor, most of these materials have been surprisingly ineffective at storing NH₃. Now, reporting in *ACS Central Science*, Yang et al. demonstrate systematically designed COFs that meet this challenge.³ Through a series of programmed modifications to the pore surface (Figure 1), the authors successfully install metal ions with open coordination sites which confer exceptional affinity for ammonia.

The challenge in capturing NH₃ is 2-fold. First, it rapidly degrades even highly stable materials, such as the Zr-carboxylate MOF UiO-66.⁴ Second, it has very low affinity for nonpolar surfaces, making the uptake capacity for NH₃ low even with high surface area materials. The current state-of-the-art sorbent for ammonia in industry is activated carbon, which has been used as a sorbent for protection from toxic gases for over a century, dating back to WWI. Although methods have been developed to impregnate carbons with various metal ions or organic functional groups, the fundamental sorbents have not changed, and the performance in terms of ammonia capacity and affinity at low relative concentrations remains poor. Carbons have a wide distribution of pore sizes, which, while advantageous for adsorbing a variety of

gases with many kinetic diameters, is not conducive to maximizing capture of a single gas.

In contrast to activated carbons, crystalline COFs and MOFs offer uniform pore size distributions and atomistic structural knowledge that can be obtained with routine X-ray crystallographic methods. The structural and compositional modularity of these materials also allows for tuning the pore size or polarity while retaining the same framework geometry, simply by using longer linkers or linkers functionalized with polar groups. Up to now, most MOF structures, especially those containing metals with open coordination sites which confer high affinity for polar molecules, have been unstable upon exposure to ammonia. Indeed, even the most well-studied MOFs for NH₃ sorption are not stable to NH₃ exposure.^{5,6} Recent studies have illuminated the impact of open metal sites on the ammonia capacity of MOFs, but only MOFs formed with the most substitutionally inert metal ions can withstand ammonia exposure.^{4,7} By contrast, imine-linked COFs offer a backbone with stronger carbon–carbon and carbon–nitrogen bonds, eliminating the often-weaker metal–ligand bonds in MOFs. Additionally, through the functionalization of nonpolar aromatic linkers with polar, acidic, or metal-binding groups, COFs can be programmed to capture coordinating and corrosive gases such as ammonia.^{8,9}

Yang et al.³ report functionalization of an imine-linked two-dimensional COF with carboxylic acid groups decorating the pore walls. Through manipulation of the amount of acid-functionalized linker, the resulting degree of acid functionalization of the resulting COF could be varied from 0% to 100%. The parent material with no additional acidic groups has an NH₃ uptake capacity of 6.85 mmol g⁻¹ at 1 bar, 298 K. This capacity increases nearly 50% to 9.34 mmol g⁻¹ for the material with 17% acid functionalization. Further introduction of acidic groups provides no additional benefit, possibly due to the steep decline in surface area, porosity, and crystallinity concomitant with the introduction of additional acid-bearing linkers.



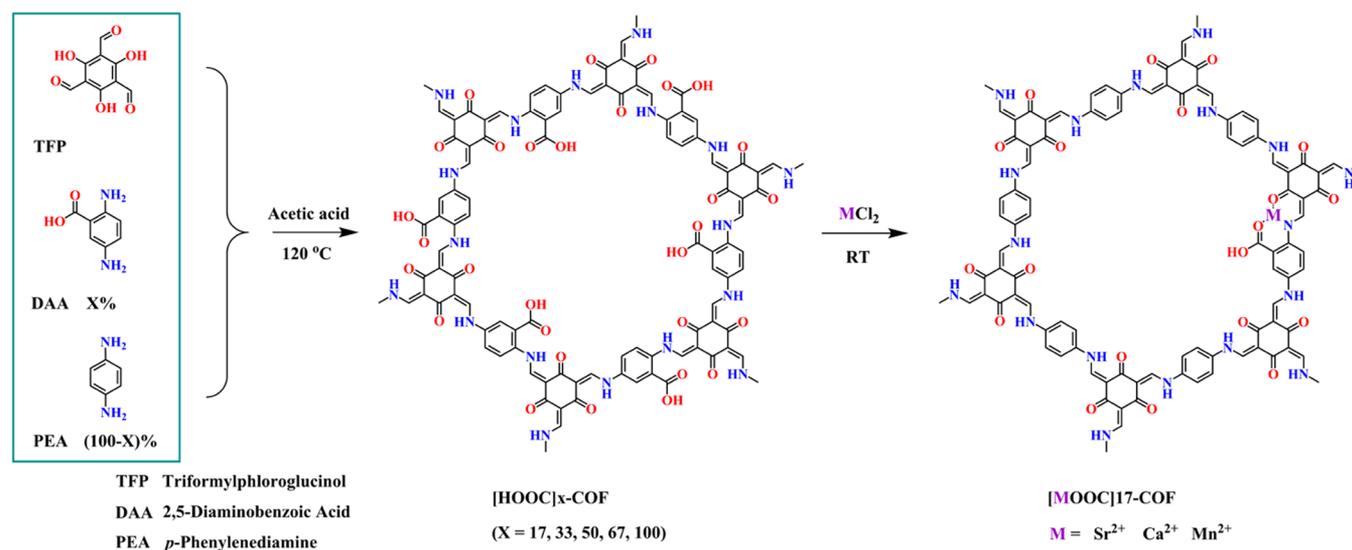


Figure 1. Synthetic route to programmable imine-linked covalent organic frameworks. Reprinted with permission from ref 3. Copyright 2018 American Chemical Society.

Encouraged by the success of their initial modification, Yang et al. proceeded to immobilize divalent metal ions in the newly formed polar binding pocket created by the carboxylic acid functionality adjacent to the imine nitrogen and additional ketone groups (Figure 1). By soaking samples of the best-performing 17% acid-functionalized COF in solutions of the respective chlorides, the authors were able to append calcium, strontium, and divalent manganese cations to the pore surface. After activation under vacuum to expose open coordination sites on the metal ions, the ammonia uptake capacity was significantly enhanced in all three cases. The strontium material was top-performing, with an equilibrium ammonia capacity of 14.30 mmol g⁻¹ at 1 bar and 298 K. This unique strategy combines the advantages of both MOFs and COFs, as the all-organic backbone provides stability, while the controlled incorporation of metal ions with accessible coordination sites confers a high affinity for ammonia.

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Besides their obvious impact for ammonia storage, these results highlight the potential utility of COFs for applications requiring extreme stability, such as flue gas streams. The fundamentally new approach toward installing open metal sites on stable COF materials will have far-reaching implications

and may inspire usage in small molecule reactivity. Further, the rational design of framework materials via stepwise synthetic transformations provides a template for future investigators seeking to program porous materials for specific applications.

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