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Phosphine Gas Adsorption in a Series of Metal–Organic Frameworks

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Supporting Information

ABSTRACT: For the first time, phosphine adsorption has been evaluated in a series of metal–organic frameworks (MOFs). Open-metal coordination sites were found to significantly enhance the ability of MOFs to adsorb highly toxic phosphine gas, with the identity of the open-metal site also modulating the amount of gas adsorbed. The MOFs studied outperform activated carbon, a commonly used material to capture phosphine.

Metal–organic frameworks (MOFs) are porous crystalline materials constructed from metal nodes and organic linkers.[1,2] The ability to modulate the organic linkers and metal nodes in these crystalline materials has resulted in a highly diverse group of porous materials.[1,2] These materials have higher surface areas[3] than conventional adsorbents, carbons and zeolites, which has resulted in a superior performance in gas storage[4] and separation applications.[5−9] This superior performance has led to MOFs being evaluated for the capture and adsorption of toxic gases[10,11] including ammonia,[12−16] arsine (AsH_3),[13] hydrogen sulfide,[17−19] and organophosphates,[20,21] with them often outperforming conventional adsorbents. These initial reports of toxic gas uptake in MOFs show that these materials have the potential to replace conventional adsorbents; however, additional studies of other toxic gases and this group of diverse materials is needed if MOFs are to realize their potential in this area.

The adsorption of phosphine (PH_3), another toxic gas of significant importance, has yet to be evaluated in MOFs. Phosphine is a highly toxic hydride gas that is utilized in a variety of applications including as a dopant in the semiconductor industry, an intermediate for the preparation of several flame retardants, a polymerization initiator, and a fumigant.[22,23] *(Note: Given the highly toxic and pyrophoric nature of phosphine, extreme care is required in its handling and usage.)* Therefore, respiratory protection against the inhalation hazards of phosphine is crucial for industrial workers and first responders. Respirators equipped with specialized filter cartridges can provide limited protection against low-risk scenarios. Chemically treated metal-impregnated activated carbons and zeolites have been investigated as sorbents in protection systems; however, they suffer from issues associated with storage capacity, aging, and degradation. Efforts to improve upon the existing carbon-based filters through rational designs are often hampered by inherent the ill-defined amorphous structure of activated carbon. Yet, the need to extend the protection time against the toxic gases while reducing the bulk of the filter cartridge remains; thus, the development of new sorbents is needed.

Herein, we report the first sorption study of phosphine in a series of MOFs (Figure 1). The adsorbents selected for this study include MOF-5[24] [$Zn_4O(C_6H_4O_4)_3$], a series of MOF-74-M[26] analogues [$M_2(C_8H_2O_6)$, where M = Cu, Mg, Co, and Mn] (Figure 1), and a broad-spectrum activated carbon. These MOFs were selected for this initial study because of their high surface area (MOF-5) and coordinatively unsaturated metal sites (the MOF-74 series), the parameters which have been important for gas adsorption and gas capture applications. Phosphine isotherms were measured for each sample and compared with a sample of activated carbon. Furthermore, nitrogen isotherms post phosphine adsorption revealed that MOF-5 and MOF-74-M maintained porosity, highlighting that the integrity of the underlying structure is retained. Cycling of phosphine was also evaluated, which showed the difference in the strength of phosphine interactions with each framework.

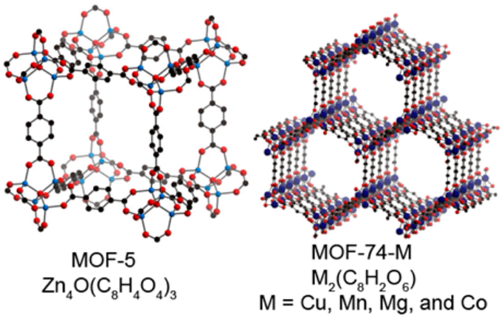

Figure 1. Crystal structures of MOF-5 and MOF-74-M. Color code: oxygen, red; carbon, black; zinc, light blue; copper, magnesium, manganese, and cobalt, dark blue. Hydrogen was omitted for clarity.

Using slightly modified procedures, MOF-5,[24] MOF-74-Co, MOF-74-Cu,[25] MOF-74-Mn, and MOF-74-Mg[26] were synthesized [see the Supporting Information (SI) for detailed synthetic procedures]. Nitrogen isotherms were measured (see Figures S7, S9, S11, and S13 in the SI), and Brunauer–Emmett–Teller

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Table 1. Physical Properties and Measured Phosphine Capacity Comparisons

sorbent	BET surface area (m^2/g)	pore volume (cm^3/g)	phosphine capacity at 0.9 bar (ads.) (mmol/g)[a]	phosphine atoms per open-metal site (ads.)	phosphine capacity at 0.006 bar (des.) (mmol/g)[b]	phosphine atoms per open-metal site (des.)
activated carbon	1040	0.81	4.37	N/A[c]	0.43	N/A[c]
MOF-5	3330	1.31	1.95	N/A[c]	0.03	N/A[c]
MOF-74-Co	1240	0.49	9.15	1.44	6.30	0.99
MOF-74-Cu	1300	0.50	4.95	0.8	3.99	0.64
MOF-74-Mn	1260	0.54	9.10	1.39	5.05	0.77
MOF-74-Mg	1300	0.53	7.80	0.95	4.40	0.54

[a] Phosphine capacities were determined at 0.9 bar upon adsorption. [b] Phosphine capacities were determined at 0.006 bar upon desorption. [c] MOF-5 and activated carbon do not contain open-metal sites.

(BET) surface areas were calculated (see Table 1). Additionally, powder X-ray diffraction (PXRD) patterns were compared to simulated patterns from single-crystal data, which confirmed the purity of each of the MOF materials (see Figures S1−S5 in the SI).

Following confirmation of the structure and activation, phosphine isotherms were measured for each material (Figure 2A). MOF-5 has the lowest uptake of phosphine (1.95 mmol/g), whereas the phosphine uptake in activated carbon was 4.37 mmol/g (Table 1 in the SI). Given the large pore volume of MOF-5 (1.31 cm^3/g) and the gradual slope of the phosphine isotherm, it is not surprising that MOF-5 has a low uptake of phosphine at workable pressures for capture systems or respirators that are operated at near-atmospheric pressures. In contrast, the isotherm of activated carbon suggests that phosphine approaches full capacity at 0.9 bar; therefore, MOF-5 may offer advantages at higher pressure. In contrast to activated carbon and MOF-5, materials that contain open-metal sites show enhanced uptake of phosphine (Table 1). MOF-74-Cu (4.95 mmol/g) exhibited the lowest capacity, followed by MOF-74-Mg (7.80 mmol/g) and MOF-74-Mn (9.10 mmol/g), and finally MOF-74-Co (9.15 mmol/g) had the highest capacity (Table 1). In addition to surpassing the phosphine capacity of the activated carbon sample used in this study, MOF-74-Co and MOF-74-Mn significantly outperform other materials including CuO/TiO_2,[27] activated carbon,[28,29] and zeolites[30,31] used for phosphine capture.

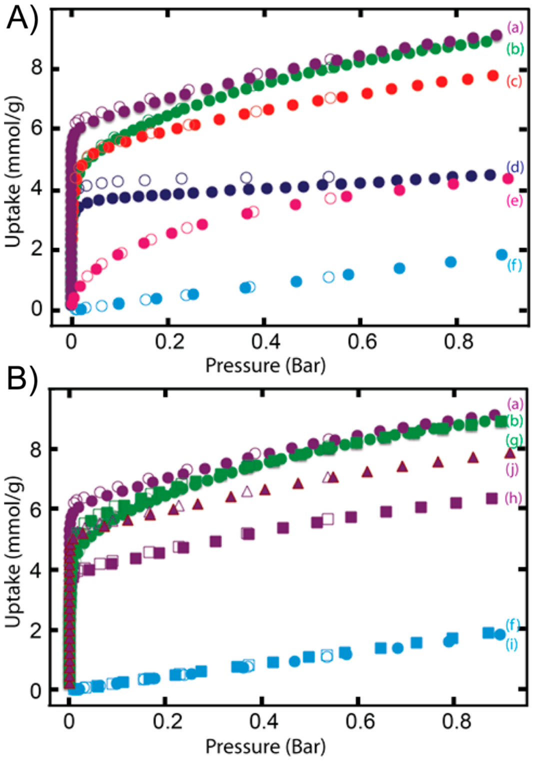

Figure 2. (A) Phosphine isotherms measured at 295 K, first run: (a) MOF-74-Co (purple), (b) MOF-74-Mn (green), (c) MOF-74-Mg (orange), (d) MOF-74-Cu (dark blue), (e) activated carbon (red), and (f) MOF-5 (light blue). (B) Cycled phosphine isotherms measured at 295 K. MOF-74-Co: (a) first isotherm (purple circles); (h) second isotherm, evacuation at room temperature (purple squares); (j) third isotherm, evacuation at 150 °C (purple triangles). MOF-74-Mn: (b) first isotherm (green circles); (g) second isotherm, evacuation at room temperature (green squares). MOF-5: (f) first isotherm (light blue circles); (i) second isotherm, evacuation at room temperature (blue squares).

In all of the MOF-74 samples studied, the majority of the captured phosphine occurs between 0 and 0.006 bar, unlike the phosphine uptake in activated carbon or MOF-5 (Figure 2A). The open-metal sites of MOF-74 have been extensively studied for the binding and adsorption of CO_2.[7] Therefore, we hypothesize that the steep uptake observed at low pressures is likely a result of binding between the Lewis basic lone pair in phosphine and the Lewis acidic open-metal sites. At 0.9 bar, there are 1.44, 0.80, 1.39, and 0.95 phosphine atoms per open-metal site in MOF-74-Co, MOF-74-Cu, MOF-74-Mn, and MOF-74-Mg, respectively (Table 1). As expected, the phosphine to open-metal site ratio drops upon desorption to 0.006 bar, equaling 0.99, 0.64, 0.77, and 0.54 phosphine atoms per open-metal site in MOF-74-Co, MOF-74-Cu, MOF-74-Mn, and MOF-74-Mg, respectively (Table 1). These results suggest a higher affinity between phosphine and cobalt than with the other metals studied.

To determine the structural integrity and recyclability of the MOFs, the two highest-performing MOFs (MOF-74-Co and MOF-74-Mn) as well as MOF-5 were evacuated at 10^{-2} Torr at room temperature for 48 h, at which point nitrogen isotherms were measured (see Figures S12−S14 and Table S1 in the SI). Surprisingly, MOF-5 and MOF-74-Mn completely retained all prior porosity and surface area (3330 and 1260 m^2/g, respectively), while MOF-74-Co regained partial surface area (1000 m^2/g). Complete retention of the surface area in MOF-5 after a phosphine isotherm is particularly interesting given the significant instability of MOF-5 when exposed to ammonia.[12]

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Following surface area measurements, phosphine isotherms were again measured (Figure 2B). As suggested by retention of the surface area through repeated nitrogen isotherms, the phosphine capacity was maintained after a second phosphine isotherm. For MOF-74-Co, the phosphine capacity dropped from 9.15 to 6.40 mmol/g. MOF-74-Co was further reactivated at 150 °C under vacuum at 10^{-2} Torr for 8 h in an attempt to recover the full performance of the material. The BET surface area improved, albeit partially, to 1155 m^2/g. As expected, the phosphine capacity also slightly improved to 7.90 mmol/g (Figure 2B). This higher energy of regeneration indicates a higher binding interaction between phosphine and cobalt than with MOF-74-Mn analogues.

In summary, open-metal sites in MOFs enhance phosphine capture at low pressures (below 0.006 bar). In particular, MOF-74-Co and MOF-74-Mn exhibit high phosphine capacity at low-pressure regimes, making these MOFs highly attractive candidates for phosphine capture particularly for respirator and abatement applications. Importantly, MOF-74-Mn can be recycled and reused after mild room temperature evacuation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01055.

> Specific synthetic procedures, PXRD, nitrogen and phosphine isotherms, sources of starting materials, and equipment used (PDF)

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Author Contributions

All experiments, including MOF synthesis, nitrogen isotherms, and phosphine isotherms, were performed at NuMat Technologies. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

Phosphine is a highly toxic and pyrophoric gas. Extreme caution is required in its handling and usage. As such, NuMat employed an automated and remotely controlled system with both actuated valves, phosphine sensors, and phosphine scrubbers.

The authors declare the following competing financial interest(s): The authors have a financial interest in NuMat Technologies, a startup company that is commercializing MOFs.

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