Long-Term Stability of MFM-300(Al) toward Toxic Air Pollutants

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ABSTRACT: Temperature- or pressure-swing sorption in porous metal–organic framework (MOF) materials has been proposed for new gas separation technologies. The high tunability of MOFs toward particular adsorbates and the relatively low energy penalty for system regeneration indicate that reversible physisorption in MOFs has the potential to create economic and environmental benefits compared with state-of-the-art chemisorption systems. However, for MOF-based sorbents to be commercialized, they have to show long-term stability under the conditions imposed by the application. Here, we demonstrate the structural stability of MFM-300(Al) in the presence of a series of industrially relevant toxic and corrosive gases, including SO₂, NO₂, and NH₃, over 4 years using long-duration synchrotron X-ray powder diffraction. Full structural analysis of gas-loaded MFM-300(Al) confirms the retention of these toxic gas molecules within the porous framework for up to 200 weeks, and cycling adsorption experiments verified the reusability of MFM-300(Al) for the capture of these toxic air pollutants.

KEYWORDS: metal–organic frameworks, toxic gases, air pollution, flue gas desulfurization, NO₂ abatement, ammonia storage, synchrotron X-ray powder diffraction

INTRODUCTION

Release of toxic gaseous air pollutants (e.g., SO₂, NO₂, and NH₃) into the atmosphere through anthropogenic activity is known to cause many health and environmental problems.¹ The capture and storage of these species are therefore of vital importance but remain a significant challenge in the development of clean air. Captured toxic gases may be of commercial value if they can be recovered via efficient storage, transportation, and release for subsequent use. Current separation and/or conversion processes often suffer from problems such as poor separation performance, lack of system regeneration, and low-value product.² Similarly, current media for toxic gas storage suffer from problems with poor storage density and high energy demand for gas compression or liquefaction.³ The use of porous materials such as zeolites,⁴ activated carbons,⁵ ionic microgels,⁶ and metal–organic frameworks (MOFs)⁷ offers the opportunity to overcome these problems by using a temperature- or pressure-swing adsorption/desorption process inside a high-capacity sorbent which can be regenerated and reused, thus minimizing the generation of waste water and solid from current processes.

A specific toxic gas separation which may be improved by using a porous sorbent is the removal of SO₂ from flue gas streams.⁸ Commonly referred to as flue gas desulfurization (FGD), this process is mainly used to remove SO₂ from the exhaust stream of coal-fired power-plants, preventing its release to the atmosphere and its contribution to acid rain and health problems.⁹ In addition, complete SO₂ removal is required as even a small amount remaining in the flue gas stream is able to react with the amine scrubbers used for CO₂ removal, leading to a permanent loss of activity and increasing running costs.⁴ The current FGD process involves the use of a lime slurry to react with SO₂ to form gypsum.¹⁰ However, not only is this product of low commercial value, but also the process requires vast quantities of water, which must undergo treatment before being released back into the environment. Furthermore, the FGD process is not able to remove 100% of the SO₂, which can then go on to poison the amine scrubbers or be released into the atmosphere. In order to utilize the captured SO₂, its reduction to elemental sulfur is required for transport, followed by reoxidation to produce sulfuric acids.¹¹

Another highly toxic air pollutant is NO₂.⁸ Mainly produced from combustion engines in motor vehicles, NO₂ can react with water to form acid rain or can be redeposited into terrestrial or marine ecosystems and contribute to eutrophication.¹² In addition to these environmental impacts, NO₂ itself is an extremely toxic gas with an OSHA ceiling limit, defined as the concentration which should not be exceeded at any time, of 5 ppm.¹³ NO₂ can also undergo an autocatalytic photochemical reaction to form toxic ground-level ozone. The
European Commission Joint Research Centre reports that global NO\textsubscript{2} emissions increased by 79% between 1970 and 2012,\textsuperscript{14,15} and therefore, the need for effective NO\textsubscript{2} capture materials is vitally important. Unlike SO\textsubscript{2} and NO\textsubscript{2}, NH\textsubscript{3} is not a byproduct of combustion and is released into the atmosphere by humans via the breakdown and volatilization of urea, most commonly from fertilizers. NH\textsubscript{3} undergoes oxidation upon heating with O\textsubscript{2} in the presence of a platinum/rhodium-based catalyst to produce commercial grade nitric acid via the Ostwald process.\textsuperscript{26} Nitric acid is an important reagent in organic synthesis, as well as being used to produce fertilizers. In addition, NH\textsubscript{3} has potential applications as a transport fuel in either combustion engines or ammonia fuel cells.\textsuperscript{37} In order to store NH\textsubscript{3} in an efficient manner, it must be liquefied by cooling to 240 K, but for applications where size is an issue, such as NH\textsubscript{3} fuel cells, the gas can be pressurized in cylinders of up to 18 bar. It has previously been shown that NH\textsubscript{3} storage in porous adsorbents can effectively overcome the energy penalty of these storage media by achieving densities close to that of liquid NH\textsubscript{3} under ambient conditions.\textsuperscript{18}

A major challenge for the use of MOFs as separation and storage media for these toxic gas species is the long-term stability of the MOF sorbents.\textsuperscript{26} SO\textsubscript{2}, NO\textsubscript{2}, and NH\textsubscript{3} are all highly corrosive, meaning that over time they may cause framework decomposition and loss of activity, leading to uncertainty and risks for their commercial use. Since their inception, the stability of MOF materials has advanced significantly,\textsuperscript{19} and several systems have been shown to be stable to multiple adsorption/desorption cycles of corrosive gases.\textsuperscript{19–27} However, the contact time of the gases with the materials in these experiments is only in the region of minutes or hours, and this does not test the stability and reactivity of these materials over the longer term. Herein, we present a long-duration synchrotron X-ray diffraction (LD-SXRD) study on a MOF material, which has been exposed to a range of corrosive gases for ca. 4 years (\textasciitilde200 weeks) with weekly collection of diffraction data (Scheme 1). This LD-SXRD experiment affords insights into the long-term stability of the material, with a view to its use in real-world gas separation and storage applications. The material chosen for this experiment was MFM-300(Al) \{Al\textsubscript{2}(\mu\textsubscript{3}-OH)\textsubscript{2}L\textsubscript{2}H\textsubscript{4}L\} = biphenyl-3,3′,5,5′-tetracarboxylic acid\}, which exhibits a 3D open framework consisting of 1D extended aluminum oxide \{Al\textsubscript{2}(\mu\textsubscript{3}-OH)\textsubscript{2}\}\text sub\text{∞} chains, linked by organic linkers in a "wine-rack" mode.\textsuperscript{27} MFM-300 materials have exhibited excellent sorption properties for NH\textsubscript{3},\textsuperscript{18} NO\textsubscript{2},\textsuperscript{34} and SO\textsubscript{2}.\textsuperscript{26–29} The aluminum analogue specifically was selected for the LD-SXRD study as it is based upon an abundant metal source and well-known crystal structure and is particularly stable within the MFM-300 series.

**EXPERIMENTAL SECTION**

Four borosilicate (0.7 mm internal diameter) capillaries (labeled A–D) were filled with a powder sample of MFM-300(Al), which was prepared according to the literature method.\textsuperscript{27} Capillary A was left open in air as a control, while capillary B was exposed to water and sealed. Capillaries C and D were placed in gas cells before being attached to a vacuum line and activated by heating at 150 °C for ca. 16 h. Capillary C was then dosed with SO\textsubscript{2} and capillary D was dosed with NH\textsubscript{3}. Two years later, two more capillaries, E and F, were loaded with desolvated MFM-300(Al). Capillary E was dosed with dry NO\textsubscript{2}, whereas capillary F was dosed with wet NO\textsubscript{2}. All capillaries except A were sealed and mounted on a stage at the I11-EH2 long-duration beamline at Diamond Light Source (UK),\textsuperscript{28} where weekly powder X-ray diffraction patterns were collected using a 25 keV beam and a 2D Pixium area detector at a sample-detector distance of ca. 0.42 m was used. No measurements were carried out during shutdowns of the synchrotron machine. A SXRD pattern of CeO\textsubscript{2} (NIST standard reference material 674b, USA) was measured before every data collection to refine the wavelength and the detector distance. The data were reduced using the DAWN software package,\textsuperscript{31,32} and all structural refinements were carried out using batch mode in TOPAS analytical software.\textsuperscript{33}

**RESULTS AND DISCUSSION**

Le Bail profile refinements were initially carried out on the diffraction data for all samples in order to obtain domain sizes and unit cell parameters (Figures S1–S6). The "week 0" data for each sample was initially refined to generate a "seed" input
file. This “seed” was then used as the input for all subsequent refinements of that sample. For all refinements after week 0, the apparent domain size was given a maximum restraint of the initially refined week 0 value in order to avoid any unphysical increases in domain size. The refined domain sizes for all samples are shown in Figure 1a. The H$_2$O-, NH$_3$- and SO$_2$-loaded samples give no change in apparent domain size and therefore no loss in crystallinity during the course of the experiment. The NO$_2$-loaded samples remain constant for the duration of the experiment, albeit with some minor fluctuations between weeks 10 and 50.

The profile refinements also produced the unit cell parameters of the MOF samples (Figure 1b). These are all around 2600 Å$^3$, in good agreement with the original value. It should be noted that gaps in data and in the plots are due to shutdowns of the synchrotron instrument. There is a significant jump (at ~25th week) in the unit cell volume of the wet NO$_2$-loaded sample. This is due to the sample being unintentionally knocked slightly during routine maintenance on the I11-EH2 beamline, causing the sample to move relative to the CeO$_2$ calibrant. Omitting this, the unit cell volume of all samples remains constant throughout the experiment, indicating the stability of the samples to these conditions. In addition to this evidence of stability, NO$_2$ (Figures S10 and S11) and NH$_3$ cycling experiments have shown little change in maximum gas uptake after 50 and 100 cycles, respectively.

Rietveld structural refinements have been carried out on the SO$_2$-, NH$_3$- and dry NO$_2$-loaded samples in order to determine changes in occupancy and binding positions of guest molecules. For all samples, a detailed structural refinement was carried out on the “week 0” diffraction data (Figures S7–S9). The results of these refinements were then used as a seed to refine all subsequent LD-SXRD data.

The refinement of the data for the NH$_3$-loaded sample at “week 0” revealed three distinct binding sites for NH$_3$ (Figure 2), consistent with those observed in the previously reported results of neutron powder diffraction refinements. For all samples, sites I and II have maximum occupancies of 1.00, and site III lies directly adjacent to a C$_2$ symmetry axis and therefore has a maximum occupancy of 0.50. The occupancies of all three sites remain constant throughout the 4 year experiment (Figure 2d), indicating that NH$_3$ has remained stored within the framework, an important property for the application of NH$_3$ storage. In
addition to the site occupancies, the interatomic distances were also established from the refinements. The framework-site I (O-N\textsuperscript{I}) distance is initially around 3.54(3) Å, indicating a strong polar interaction between site I and the hydroxyl group of the framework. This distance gradually increases by around 3.0% over the course of the experiment to a final value of 3.66(5) Å. The hydrogen bonding chain is continued to NH\textsubscript{I}, which sits at an initial distance of 2.86(4) Å. This distance is slightly shorter than both the optimal N-N distance determined by \textit{ab initio} calculations [3.385(2) Å]\textsuperscript{34} and the shortest distance observed in solid ammonia [3.380(4) Å].\textsuperscript{35} This discrepancy is possibly due to the confinement effect of the MOF pore. This N\textsuperscript{I}-N\textsuperscript{II} distance does not change over the course of the refinement, within error. NH\textsuperscript{II} is also in the hydrogen bonding range of NH\textsuperscript{I}, with an initial N\textsuperscript{II}-N\textsuperscript{III} distance of 2.97(7) Å, which remains constant throughout the experiment. The intermolecular bonding geometry of the three ammonia sites does not match perfectly with the geometry, which may be predicted based purely on the angles between hydrogen atoms and lone pairs. However, it has been shown by both \textit{ab initio} calculations and diffraction studies that even the hydrogen bonds in solid NH\textsubscript{3} are not perfectly linear,\textsuperscript{34,35} as they are in water ice (I\textsubscript{h}).\textsuperscript{36}

The initial structural refinement of the “week 0” data reveals two binding sites for SO\textsubscript{2}, with SO\textsubscript{2}\textsuperscript{I} located near to the bridging hydroxyl of the MOF and SO\textsubscript{2}\textsuperscript{II} located more centrally in the pore channel and displaying polar interaction with SO\textsubscript{2}\textsuperscript{I}, with initial occupancies of 0.43 for site I and 0.41 for site II (Figure 3). Both occupancies decrease gradually throughout the experiment to occupancies of 0.39 for site I and 0.37 to site II, with drops of 9 and 10%, respectively. This may be due to the SO\textsubscript{2} molecules either becoming disordered within the pore of the MOF or leaving the framework entirely and filling the intercrystalline cavities within the capillary. This loss of ordered SO\textsubscript{2} is less of an issue because of the intended application of SO\textsubscript{2} separation requiring the SO\textsubscript{2} to be retained within the MOF for a relatively short time to allow the safe transport, compared to NH\textsubscript{3} storage where NH\textsubscript{3} may be held within the MOF for extended periods of many weeks or months. The SO\textsubscript{2}-framework (O-O) distance has an initial value of 3.43(3) Å, indicating a strong hydrogen bond between the hydroxyl group of the MOF and the oxygen of SO\textsubscript{2}. The distance between the two SO\textsubscript{2} sites (S-S) has an initial value of 3.36(4) Å, demonstrating the strong polar interaction between the SO\textsubscript{2} molecules within the pore. There is a 2% decrease in the framework-SO\textsubscript{2}\textsuperscript{I} (O-O) distance during the experiment which is accompanied by a 2% increase in the SO\textsubscript{2}\textsuperscript{I}-SO\textsubscript{2}\textsuperscript{II} distance. By comparing the initial and final positions of the SO\textsubscript{2} molecules (Figure 3d), it can be determined that these small changes are the result of the SO\textsubscript{2} site translating to a more central position over the bridging hydroxyl of the MOF. This is a sign of the SO\textsubscript{2} site relaxing into a more energetically favorable position.

Finally, Rietveld refinements were carried out on the SXRD data of dry NO\textsubscript{2}-loaded samples (Figure 4). Initial refinement revealed one NO\textsubscript{2} binding site adjacent to the bridging hydroxyl of the MOF and one N\textsubscript{2}O\textsubscript{4} dimer located more

Figure 3. a) Refined binding sites for SO\textsubscript{2} at “week 0”; (b) idealized representation of binding interactions of SO\textsubscript{2}\textsuperscript{I} and SO\textsubscript{2}\textsuperscript{II}; (c) view along the pore of SO\textsubscript{2}@MFM-300(Al); (d) comparison of refined binding positions for SO\textsubscript{2} at week 0 (green) and week 182 (blue); (e) refined occupancies for SO\textsubscript{2} throughout the experiment; (f) refined SO\textsubscript{2} interaction distances throughout the course of the experiment.

Figure 4. a) Refined binding sites for NO\textsubscript{2} at “week 0”; (b) idealized representation of NO\textsubscript{2}\textsuperscript{I} and NO\textsubscript{2}\textsuperscript{II} binding interactions; (c) view along the pore of NO\textsubscript{2}@MFM-300(Al); (d) comparison of refined binding positions for NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} at week 0 (green) and at week 120 (blue); (e) refined occupancies for NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} throughout the experiment; (f) refined NO\textsubscript{2} interaction distances throughout the course of the experiment, including both N\textsubscript{2}O\textsubscript{4}-NO\textsubscript{2} interaction distances (light and dark blue).
centrally in the pore, as observed previously. The NO$_3$ site has an initial occupancy of 0.50, which remains constant over the course of the 120 week period. The N$_2$O$_4$ dimer has an initial occupancy of 0.29, which also remains around the same value for the duration of the experiment. The framework–NO$_2$ (O–O) distance has an initial value of 3.75(3) Å, which, after a small decrease, remains constant for the 120 week period. The NO$_2$–N$_2$O$_4$ (N–O) distances have initial values of around 2.85(2) Å, which increase by around 10% after the first 10 weeks before remaining stable at around 3.15(3) Å. By comparing the initial and final positions of the NO$_2$ and N$_2$O$_4$ molecules (Figure 4), we can see that this is the result of a simultaneous rotation of both the NO$_2$ molecule and its dimer within the pore of MFM-300(Al). Overall, no framework phase change or decomposition was observed for NO$_2$-loaded MFM-300(Al) over the experiment. Rietveld refinements were not carried out on the wet NO$_2$ data as the presence of both NO$_2$ and H$_2$O molecules would make the definitive assignment of electron density in the MOF pore not possible.

## CONCLUSIONS

Powerful drivers exist to explore the long-term stability of MOF materials under operational conditions and in contact with corrosive substrates to promote their future applications in industry. We have demonstrated the stability of a promising MOF sorbent, MFM-300(Al), to a range of toxic air pollutants over an extended time period (~4 years). Le Bail refinements of SXRD data have shown that there is no decrease in the apparent domain sizes or change in the unit cell volumes over the course of the experiment. Rietveld refinements of the gas-loaded MOF samples have shown that MFM-300(Al) is able to store ammonia and nitrogen dioxide for at least 183 and 120 weeks, respectively, and that there is only a small decrease in the amount of sulfur dioxide present over a 183 week period. The study provides a unique structural insight into MOF-based sorbents for future applications in capture and storage of toxic gas air pollutants.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c11134.

Experimental details, Le Bail and Rietveld refinements, NO$_3$ cycling data, and additional NO$_2$ stability data (PDF)

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