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1 Investigating the cheletropic reaction between sulfur dioxide and
2 butadiene-containing linkers in UiO-66.

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Draft

Abstract

UiO-66 and a muconic-acid-functionalized derivative of UiO-66 (UiO-66-MA) were synthesized *via* the solvothermal method to determine if the muconic acid could undergo a cheletropic reaction in the presence of sulfur dioxide inside the MOF. Both MOFs were exposed to a constant flow of sulfur dioxide, and UiO-66-MA was observed to take up three times more sulfur dioxide than unfunctionalized UiO-66. Despite the improved uptake of sulfur dioxide in UiO-66-MA, NMR and IR data indicate that no chemical change occurred to the muconic acid indicating that a cheletropic reaction did not occur. We thus propose that the increased adsorption is either due to an interaction between the sulfur dioxide and un-bound carboxylic acid from the muconic acid or a favourable interaction between the butadiene of muconic acid and sulfur dioxide.

Key words: sulfur dioxide; adsorption; UiO-66; breakthrough; metal-organic frameworks;

Introduction

Sulfur dioxide is a by-product of fossil fuel burning. Under humid environments, sulfur dioxide rapidly reacts with water (e.g., in the atmosphere or lungs) to form sulfuric acid. As such, along with ammonia, chlorine, and hydrogen sulfide, sulfur dioxide is considered to be a toxic industrial chemical (TIC).¹ TICs are often used in chemical warfare due to the ease in which they can be obtained for commercial applications, unlike nerve agents.² For example, sulfur dioxide gas is primarily used for production of sulfuric acid, as an oxidising agent to reduce hydrogen sulfide to elemental sulfur, and even as a fruit preservative.³ Considering the risks of sulfur dioxide to individuals, society (e.g., destruction of art due to acid rain), and the environment, it is critical to find methods of reducing anthropogenic sulfur dioxide as well as developing methods to protect individuals from weaponised sulfur dioxide.⁴

Adsorption can be classified into two major categories, chemisorption and physisorption.⁵ Sulfur dioxide physisorption primarily occurs through van der Waals interactions. In this case, the adsorbent is non-specific to the analyte being adsorbed with regeneration of the adsorbent being accomplished *via* mild heating, vacuum, or even flowing another gas through the material. In chemical adsorption, the adsorbent is specific to the analyte (sulfur dioxide herein).⁶ The sulfur dioxide is chemically bound to the adsorbent such that it cannot be easily removed. Depending on the application, chemical or physical adsorption may be preferred. For chemical separation in industrial processes, physical adsorption may be preferred so that the adsorbent can be easily regenerated rather than replaced, and the sulfur dioxide can be subsequently utilized as a value-added product to industry. However, when it comes to human health protection (e.g., civilians and soldiers), chemisorption is typically a better option.

Another key requirement of a good adsorbent is the available surface area for the adsorbate to adsorb onto. The larger the surface area of the adsorbent, the shorter the geometric path length needs to be for efficient removal. For this reason, high surface area architectures such as nanoparticles,⁷⁻¹⁰ opal/inverse opal arrays,¹¹ fibrous materials such as aerogels,¹²⁻¹⁵ activated carbons,¹⁶⁻²⁰ and zeolites²¹⁻²⁴ have all been featured in chemical separations. In addition to these high surface area materials, one class of materials that has illustrated the greatest potential for the removal of TICs is metal-organic frameworks (MOFs), such as UiO-66,²⁵⁻²⁸ UiO-67,²⁹ MOF-74,³⁰ and NU-1000,³¹ to name a few.³²⁻³⁸

MOFs are a class of porous materials made by linking metal cations/clusters (nodes) *via* organic molecules (linkers) that possess two or more metal-binding moieties (e.g., pyridine, imidazole, carboxylic acids) that promote metal bridging vs. metal chelation. The advantage of

MOFs over other high surface area porous materials, is that the node and/or linker can be tuned for a desired application.^{32,33,39-42}

In the present manuscript, we turned our attention to tuning MOFs toward sulfur dioxide sequestration *via* chemisorption. As shown in Scheme 1, 1,3-butadiene, and derivatives of 1,3-butadiene, have been shown to undergo a cheletropic addition of sulfur dioxide to form a butadiene sulfone (sulfolene).⁴³⁻⁴⁵ This cheletropic reaction is known to be reversible under elevated temperature.^{43,46,47} Thus, we hypothesized that incorporation of 1,3-butadiene into a highly porous structure may improve the removal of sulfur dioxide. Furthermore, the material may be regenerated for additional uses. One potential linker that would allow us to investigate this chemistry is *trans,trans*-muconic acid. Specifically, as has been previously demonstrated by others,⁴⁸ muconic acid was incorporated into a highly stable Zr-containing MOF (UiO-66; Figure 1) *via* solvent assisted ligand exchange (SALE),^{49,50} allowing a study of the role this MOF has on sulfur dioxide sequestration.

Scheme 1 Reaction between 1,3- butadiene and sulfur dioxide to form a butadiene sulfone.

70

71 Figure 1 (a) $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$ cluster showing 4 of 12 μ -BDC units. (b) Schematic drawing of UiO-66. (c)
 72 Schematic drawing of UiO-66-MA illustrating how the organic linkers were partly replaced by muconic
 73 acid.

74 Experimental

75 General procedures, materials, and instrumentations

76 All compounds and solvents were used as received: deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$;
 77 Cambridge, 99.5%), deuterated sulfuric acid ($\text{D}_2\text{SO}_4/\text{D}_2\text{O}$; Aldrich, 99.5 atom% D), ethyl alcohol
 78 (Aldrich, denatured), hydrochloric acid (Caledon, 38%), methanol (ACP, 99.8%), *N,N*-
 79 dimethylformamide (DMF; Fisher, 99.9%), potassium hydroxide (ACP, 85%), terephthalic acid
 80 (H_2BDC , Aldrich, 98%), *trans,trans*-muconic acid (Aldrich, 98%), zirconium(IV) chloride (Aldrich,
 81 99.5%).

82 Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku X-ray Ultima IV
 83 diffractometer equipped with a copper X-ray source and a scintillation counter detector.

84 N_2 gas adsorption isotherm data was collected at 77 K on a TriStar II PLUS surface area and
 85 porosity analyzer. All the samples were activated before each isotherm by heating the samples
 86 at 80 °C under vacuum for approximately 8 h.

¹H NMR experiments were performed on a 300 MHz Bruker Advance III 300 instrument. Samples were digested in a few drops of D₂SO₄ followed by the addition of ca. 1 mL of DMSO-*d*₆ solution as the lock-solvent; all solutions were filtered before measurements.

Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) experiments were carried out on a Bruker Tensor 27 FT-IR with a Bruker Platinum ATR accessory equipped with a single reflection diamond crystal. Sample was scanned between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹ and the final spectra was the average of 16 scans.

Microbreakthrough testing was done as previously reported.³⁰ A sulfur dioxide gas concentration of 1000 mg/m³ flowed at 20 mL/min was used at 20 °C under dry conditions (dew point = -40 °C). Samples were loaded into a 4 mm i.d. fritted glass tube to a depth of approximately 4 mm corresponding to a volume of approximately 50 mm³ giving a retention time of 0.15 s. Breakthrough concentrations were measured on a Gas Chromatography (GC) using a flame photometric detector (FPD).

Synthesis

UiO-66 was synthesized from DMF as previous reported.⁵¹

The synthesis of UiO-66-MA was made through SALE of UiO-66.^{49,52-54} In short, 106.6 mg (0.75 mmol) *trans,trans*-muconic acid was dissolved in 8 mL of a 4% KOH solution *via* sonication before being neutralized to pH=7 with 1 M HCl. To the solution was added 150 mg (0.75 mmol assuming no linker defects) of UiO-66. The mixture was stirred to finely disperse the UiO-66 particles before being heated at 85 °C in an oven for 5 d. The resulting solid was washed first with 3 × 10 mL of methanol to remove any dissolved linker. Subsequently, the solvent was

replaced daily with fresh methanol for 3 d before being vacuum filtered. After filtration, the sample was dried under a vacuum for 8 h at 60 °C, yielding a light-yellow powder.

Results and discussions

UiO-66 and UiO-66-MA were made according to literature methods as outlined in the experimental section. To ensure that the MOF remained intact after the linker incorporation, the PXRD of UiO-66 and UiO-66-MA were measured and compared to the simulated spectrum of UiO-66. As can be seen in Figure 2, the diffractogram of both UiO-66 and UiO-66-MA are identical indicating that the structure of the crystalline materials is consistent with the structure of UiO-66. Given the strong similarities between the diffractograms in Figure 2 and by Férey,⁵⁵ the *trans,trans*-muconic acid likely undergoes a *cis/trans* isomerization.

Figure 2 Simulated UiO-66 (black bottom), observed UiO-66 (red middle), and UiO-66-MA (blue top), powder X-ray diffraction patterns.

To confirm the formation of UiO-66-MA from UiO-66, the ¹H NMR of an acid-digested sample of UiO-66-MA was measured. As seen in Figure 3, UiO-66-MA not only showed the terephthalic acid peak at 7.95 ppm, but also the muconic acid peaks at 6.27 and 7.27 ppm,

respectively, with an integration ratio of 1.00:0.34 BDC:muconic acid; the combined integration of both muconic acid peaks equaled 0.34 ppm. This indicates that there is a 1 to 3 ratio of muconic acid to terephthalate linkers. Alternatively, of the total number of linkers, roughly 25% of the linkers are muconic acid. Lastly, we further measured the gas-adsorption isotherms in order to confirm that the muconic acid linker was incorporated into the MOF instead of simply being trapped in the pore. To that end, the N₂ gas-adsorption isotherms of UiO-66 and UiO-66-MA were measured at 77 K. As shown in Figure 4, the gas adsorption isotherms for UiO-66 and UiO-66-MA are similar; the Brunauer-Emmett-Teller (BET) surface area observed of UiO-66 and UiO-66-MA was 1200 and 1000 m²/g, respectively.

Figure 3 ¹H NMR spectrum of UiO-66-MA(blue-top), UiO-66 (red-middle), and trans,trans-muconic acid (green-bottom).

136

137 *Figure 4 Nitrogen adsorption isotherms of UiO-66(red) and UiO-66-MA(blue) measured at 77 K.*

138 With UiO-66-MA in hand, a micro-breakthrough experiment was carried out using a 1000
 139 mg/m³ sulfur dioxide concentration. Each MOF was exposed to the challenge concentration *via*
 140 a 20 mL/min flow rate using dry nitrogen as the carrier gas. Sulfur dioxide micro-breakthrough
 141 and desorption curves are shown in Figure 5 and summarized in Table 1. The quantity of
 142 adsorbed sulfur dioxide at constant flow (i.e., the dynamic loading) can be calculated from the
 143 area above the curve between $t = 0$ and the breakthrough time ($C/C_0 = 1$). From this data, UiO-
 144 66 and UiO-66-MA exhibited an effective loading of 0.18 and 0.58 mol/kg, respectively. UiO-66-
 145 MA showed better than 3 times increase in sulfur dioxide adsorption than the parent MOF.
 146 Considering the maximum loading is 0.9 mol/kg for UiO-66-MA, assuming no linker defects⁵⁶⁻⁶³
 147 exist in the MOF and every muconic acid reacts with one sulfur dioxide, then sulfur dioxide is
 148 able to interact with 64 % of the active sites before breakthrough.

Figure 5 Sulfur dioxide micro-breakthrough and desorption curves under dry condition for UiO-66 (red) and UiO-66-MA (blue).

Table 1 Dynamic loading of sulfur dioxide on UiO-66 and UiO-66-MA

	Sorbent mass (mg)	Effective loading (mol/Kg)
UiO-66	9.3	0.18
UiO-66-MA	11.5	0.58

Given that the sulfur dioxide desorbed so easily, the data in Figure 5 indicates that at least some of the sulfur dioxide is physically adsorbed in the pore rather than undergoing the cheletropic reaction shown in Scheme 1. In order to probe the chemistry of how sulfur dioxide is incorporated into UiO-66 vs. UiO-66-MA, we measured the IR of the two MOFs before and after gas adsorption. As shown in Figure 6 and Figure 7, there is no significant change in the IR spectrum in either MOF before or after the breakthrough measurements. If chemisorption was to occur, then it would be expected that new peaks at ca. 1300-1100 cm^{-1} would be observed for UiO-66-MA.⁶⁴

162

163 *Figure 6 FT-IR of UiO-66 before (red bottom) and after (purple top) sulfur dioxide adsorption.*

164

165 *Figure 7 FT-IR of UiO-66-MA before (blue bottom) and after (green top) sulfur dioxide adsorption.*

166 To further examine the reaction between sulfur dioxide and UiO-66-MA, UiO-66-MA was
167 digested in D₂SO₄/DMSO-*d*₆ to investigate any change to the muconic acid *via* ¹H NMR. As
168 shown in Figure 8, the spectrum of UiO-66-MA before and after sulfur dioxide exposure remain
169 unchanged, again indicating that sulfur dioxide is most-likely physically adsorbed and not
170 chemically reacted with the muconic acid.

171

Figure 8 ^1H NMR spectrum of UiO-66-MA, before (blue-bottom), and after (green top) sulfur dioxide sequestration.

Given the data presented herein, under these reaction conditions, UiO-66-MA does not undergo a cheletropic reaction with sulfur dioxide. However, the muconic acid does participate in sulfur dioxide adsorption. In the presence of the muconic acid-containing MOF, there is a 3-fold increase in dynamic sulfur dioxide adsorption. With that in mind, we propose that there may be insufficient energy available to undergo the cheletropic reaction leading to an interaction, rather than a bond, between sulfur dioxide and muconic acid. Alternatively, DeCoste and co-workers have demonstrated that oxalic acid modified UiO-66 is capable of increasing the sulfur dioxide adsorption.²⁸ In our system, we do not observe any changes in the IR spectrum of UiO-66-MA before/after sulfur dioxide adsorption, as was observed for the oxalic acid-modified UiO-66. This may be due to the complete desorption of sulfur dioxide prior to IR measurements. However, we cannot rule out that residual terminal carboxylate units, left behind by incomplete muconic acid incorporation (i.e., the attachment of only one of the two carboxylate groups), are able to interact with sulfur dioxide in order to increase adsorption.

188 Further examination of the temperature dependence of UiO-66-MA and related 1,3-diene-
189 containing MOFs to the cheletropic reaction with sulfur dioxide is ongoing.

190 Conclusions

191 We compared the ability of two MOFs to adsorb sulfur dioxide under dynamic conditions to
192 determine if a cheletropic reaction between sulfur dioxide and muconic acid were possible
193 under standard conditions. A nearly 3-fold increase in sulfur dioxide adsorption was observed
194 for the MOF possessing muconic acid over the muconic acid-free MOF. Despite the improved
195 uptake, however, there was no indication of a chemical reaction between the two species.
196 Instead, sulfur dioxide preferred to interact with the MOF in a physisorption fashion. The
197 underlying mechanism of adsorption is being examined.

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201 Notes

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