Our extensive work on water adsorption of MOFs has led to understanding the stability problem in a holistic way, while examining methods to create MOFs with molecule-specific adsorption sites. As a result of this work, the thousands of MOFs reported in the literature can be more easily categorized for possible application in water-containing separations by evaluating the coordination environment and classifying the steric contributions from the linker. A main focus of this overall work was to evaluate MOFs for selective removal of ammonia from air. We found that UiO-66-OH has a capacity of ~5.7 mmol/g for ammonia under dry conditions, which is close to...
ABSTRACT

Our extensive work on water adsorption of MOFs has led to understanding the stability problem in a holistic way, while examining methods to create MOFs with molecule-specific adsorption sites. As a result of this work, the thousands of MOFs reported in the literature can be more easily categorized for possible application in water-containing separations by evaluating the coordination environment and classifying the steric contributions from the linker. A main focus of this overall work was to evaluate MOFs for selective removal of ammonia from air. We found that UiO-66-OH has a capacity of ~5.7 mmol/g for ammonia under dry conditions, which is close to ammonia removal goal of 6 mmol/g. However, we observed a decrease in the ammonia capacities of functionalized UiO-66 variations under humid conditions. The variants functionalized with –COOH groups were evaluated for potential metal insertion sites for copper coordination. These new materials were shown to exhibit dynamic ammonia capacities of 6.8 and 6.4 mol/kg under dry and humid conditions, respectively. These capacities exceeded our project target of 6 mol/kg. Overall, it was established that balancing water adsorption behavior and high selectivity and high capacity for ammonia is crucial to developing new adsorbents for ammonia removal from air.
Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received | Paper
---|---


09/12/2013 18.00 | Himanshu Jasuja, Ji Zang, David S. Sholl, Krista S. Walton. Rational Tuning of Water Vapor and CO2 Adsorption in Highly Stable Zr-Based MOFs, The Journal of Physical Chemistry C, (11 2012): 0. doi: 10.1021/jp308657x


09/30/2015 32.00 | Himanshu Jasuja, Gregory W. Peterson, Jared B. Decoste, Matthew A. Browe, Krista S. Walton. Evaluation of MOFs for air purification and air quality control applications: Ammonia removal from air, Chemical Engineering Science, (03 2015): 0. doi: 10.1016/j.ces.2014.08.050


TOTAL: 21

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(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper


TOTAL: 1
Number of Papers published in non peer-reviewed journals:

(c) Presentations

See attachment

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

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TOTAL:

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Patents Awarded

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The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ......
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......

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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer
SUMMARY OF RESEARCH ACTIVITY

A major goal of this project was to evaluate MOFs for use in air purification systems. Our extensive work on water adsorption of MOFs has led to understanding the stability problem in a holistic way, while examining methods to create MOFs with molecule-specific adsorption sites. As a result of this work, the thousands of MOFs reported in the literature can be more easily categorized for possible application in water-containing separations by evaluating the coordination environment about the metal site in the structure and classifying the steric contributions from the linker. A main focus of this overall work was to evaluate MOFs for the selective removal of ammonia from air. We successfully synthesized new variants of UiO-66 (UiO-66-OH, UiO-66-(OH)₂, UiO-66-NO₂, UiO-66-NH₂, UiO-66-SO₃H, and UiO-66-(COOH)₂) for enhanced interactions with ammonia. We found that UiO-66-OH has a capacity of ~5.7 mmol/g for ammonia under dry conditions which is very close to ammonia removal goal of 0.1 g/g MOF (or ~ 6 mmol/g). However, we observed a decrease in the ammonia capacities of functionalized UiO-66 variations under humid conditions due to competition between water and ammonia molecules for adsorption on the active sites. The variants functionalized with –COOH groups were evaluated for potential metal insertion sites. Copper was coordinated to these free functional groups to create UiO-66 with copper atoms attached to the functional groups throughout the material. As a result of these metal sites, the new materials were shown to exhibit dynamic ammonia capacities of 6.8 and 6.4 mol/kg under dry and humid conditions, respectively. These capacities exceeded our project target of 6 mol/kg. Overall, it was established that balancing the water adsorption behavior and high selectivity and high capacity for ammonia is crucial to developing new adsorbents for ammonia removal from air.

MOFs are synthesized by self-assembly of organic ligands with metal groups, which allows for unprecedented control over pore size and chemical functionality of the internal pore surface. A major thrust in our group over the past five years has been to uncover a fundamental understanding of the features that control the stability of MOFs upon exposure to water. Water sensitivity is a major weakness of MOFs compared to conventional adsorbents, and identifying the parameters that contribute to this sensitivity is critical for developing MOFs for large-scale applications.

Work in our lab has focused primarily on uncovering the structural factors and mechanisms that contribute to stability or instability of MOFs. The criteria developed as a result of this work have important implications for future MOF synthesis efforts. Prof. Walton is one of the few researchers in the world to focus on this topic, and her group has published prolifically in this area (18 articles since 2012). As a result, she has gained an international reputation for her work, and her papers have already been cited over 350 times.

Our first article on this topic was published in 2012 (Schoenecker 2012), and was among the first in the field. It has been cited over 100 times and has been designated a “Highly Cited Paper” by Web of Knowledge, which means that the paper has “received enough citations to place it in the top 1% of its academic field based on a highly cited threshold for the field and publication year.” This work provided one of the first systematic investigations of water adsorption in prototypical MOFs and showed that in some cases, these materials display water adsorption behavior that is comparable to conventional adsorbents such as zeolites and activated carbon.

Since that first article in 2012, we published a series of papers on water adsorption in a set of structures in the DMOF family (a pillared MOF synthesized using zinc salts, DABCO, and terephthalic acid (BDC) that can be functionalized in a variety of ways). These articles showed, for the first time, that it is possible to adjust the water stability of a pillared MOF both in the positive and negative directions by proper functionalization of the BDC ligand (Jasuja 2012, 2013). Further work on this MOF family introduced the important distinction between kinetic and thermodynamic water stability, and we described experimental evidence for a kinetically governed water stability mechanism in these MOFs. In addition, molecular simulations showed the reason for the improvement in kinetic stability is due to shielding of the carboxylate oxygen in the DMOF-TM2 structure by tetramethyl groups, which prevents hydrogen bonding interactions and subsequent structural transformations from occurring (Jasuja 2013).

Our extensive work in this field culminated in a recent comprehensive review article published in Chemical Reviews (impact factor of 45) in October 2014. In this review, we develop criteria for establishing two types of stability: thermodynamic stability (TS) and kinetic stability (KS). As shown in Figure 1, there are several factors and mechanisms assigned to these types. MOFs with TS will have high metal-ligand bond strength and lower binding energies with water. For the MOFs, the irreversible hydrolysis reaction is
unfavorable for any water loading. Exposure to water vapor vs. liquid water will also not impact the stability result.

Figure 1. Flowchart of structural factors governing water stability in MOFs. (Figure taken from Burtch et al. 2014).

Kinetically stable MOFs are more complex in mechanism and in governing properties. In general, we have found that materials with high hydrophobicity are stable to water vapor exposure because water molecules are unable to cluster at the metal cluster. Steric factors also are important. In this case, the governing properties are i) how easily the water can approach the metal site and ii) how easily displaced the ligand is.

Based on this information, we proposed three methods for improving the water stability of MOFs. These are shown in Figure 2. Metal-ligand bond strength can be improved by metal-ion doping. Steric factors such as catenation and ligand functionalization can be used to limit the accessibility of water and lock ligands into place. Enhancement of the MOFs hydrophobicity and stability can be enhanced through plasma-enhanced chemical vapor deposition, ligand functionalization, and core-shell strategies.

As a result of this work, the thousands of MOFs reported in the literature can be more easily categorized for possible application in water-containing separations by evaluating the coordination environment about the metal site in the structure and classifying the
steric contributions from the linker. Notably, this work provides guidelines and criteria that will aid synthesis efforts to create robust MOFs with water adsorption behavior that is comparable to a range of conventional adsorbents such as zeolites and activated carbons. This work will be extremely valuable for both the MOF community and the broader adsorption and porous materials communities.

The work on water stability was co-supported with funds from Walton’s PECASE award (expired). Leveraging these efforts allowed the addition of multiple personnel to tackle this important topic, and broadened our coverage of materials and conditions. As a result, structure-property relationships could be developed.

Figure 2. Mechanisms and experimental approaches for improving the water stability in existing MOFs. All mechanisms are directly related to the structural factors discussed in Figure 1. (Figure taken from Burtch et al. 2014)
2. MOFs as Ammonia Adsorbents

Nanoporous materials play a crucial role in providing protection against toxic industrial chemicals (TICs) in both military and non-military applications. The impregnated activated carbon used in this application performs well in removing low vapor pressure compounds from air, but it is not effective in filtering high vapor pressure gases (> 100mmHg) such as ammonia (NH₃), carbon monoxide, and sulfur dioxide. The solution to this problem requires the development of novel materials that represent a radical departure from traditional adsorbents such as activated carbons and zeolites. The objective of this portion of work in this area has been to develop an engineered material that is capable of adsorbing ammonia from an ambient air stream at loadings of 6 mol/kg.

Over the past three years, Prof. Walton has been leading the development of the metal-organic framework “UiO-66” as a platform for air purification systems. This material is robust and stable under humid and corrosive environments and can be tailored with a variety of functional groups (Cmarik 2012). Prof. Walton and her research group successfully synthesized six new variants of UiO-66 for enhanced interactions with ammonia (Jasuja 2015). Many of these materials were found to adsorb ammonia effectively, and UiO-66-OH displayed a capacity of ~5.7 mol/kg for ammonia under dry conditions, which is near the ammonia removal goal of 6 mol/kg. This is the highest loading ever achieved for ammonia in MOFs that do not possess open metal sites. These encouraging results set the course for synthesis scale up of UiO-66 and development of engineered forms.

![Figure 3. NH₃ breakthrough curves under humid (80% RH) conditions at a feed concentration of 1000 mg/m³ (1438 ppm) and temperature of 298 K. (Figures from Jasuja et al. Chem Eng Sci, 2015)](image)

A common issue with synthesized MOFs is that they are usually produced as small crystals or powders. These powders are often not suitable for fixed-bed systems due to large pressure drops and inefficient packing densities. In spite of the importance of these issues, pelletization of MOFs has been understudied in the field to date. Prof. Walton’s research in this area seeks to fill these knowledge gaps. In collaboration with G. Peterson at Edgewood Chemical Biological Center (ECBC), Prof. Walton’s research has shown that two MOFs, Cu-BTC and UiO-66, form good quality pellets without the need of any binder (Peterson 2013). Pellets were pressed at 1000 and 10,000 psi and tested for ammonia breakthrough adsorption capacities. The
adsorption properties of Cu-BTC pellets remained consistent with the properties displayed by the powder form, and UiO-66 pellets showed only a slight decrease in adsorption behavior.

The research labs of Prof. Walton have also developed unique expertise in the scale-up of MOF synthesis (Schoenecker 2013). Prof. Walton’s solvent reduction technique has led to a more than 100-fold increase in the production of UiO-66. For example, these new synthesis methods yield 50 grams of this MOF using the same reaction volume that previously yielded only 0.5 grams.

3. Metal Insertion for Introducing Stable Open Metal Sites into MOFs

3.1: Metallation of UiO-66-COOH and –(COOH)₂

Work has been ongoing to use post-synthetic modification (PSM) to create metal-carboxylate groups in water stable UiO-66 and test its performance towards ammonia capture from air. Our approach is summarized below.

- Synthesis of UiO-66 with –COOH and –(COOH)₂ functional groups (ligands shown at right)
  - Insertion of secondary metal (Cu) into the framework by PSM
  - Characterization
    - PXRD, N₂ physisorption, metal content analysis, XPS
  - NH₃ breakthrough studies (wet and dry conditions)  

Schematic 1: BDC Ligands

The MOF was synthesized following previously established procedures. Copper was inserted by mixing the activated MOF with 10 mL of 0.1M CuCl₂ in DMF (shown in the schematic below). Surface areas were consistent with previous work. Analysis using ICP-MS was performed to determine metal content. These results are shown below in Table 1.

Schematic 2: Metal insertion into UiO-66-COOH

<table>
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<th>MOF</th>
<th>Copper Loading, Cu/Zr (Mass Ratio)</th>
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<td></td>
<td>Theory</td>
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<tr>
<td>UiO-66-COOCu</td>
<td>0.70</td>
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<tr>
<td>UiO-66-(COOCu)₂</td>
<td>1.39</td>
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</table>
A few important points were observed:
- Entry of metal ions into the frameworks is restricted by the low pore space available for metal complexation
- Higher copper loadings for –COOH than for –(COOH)₂
- Only –COOH groups on the crystal surface undergo coordination
- High water loadings at low relative humidities (Figure 4)
- Type I Isotherm
- Similar behavior to UiO-66-(COOH)₂
- Affinity of metal cations towards water
- Low hysteresis

In general, it is possible that we have only added metal to the surface of crystal; it is so far unclear how much Cu loading occurs inside the pores; these studies are ongoing.

![Figure 4: Water adsorption isotherms on metallated samples at 298 K.](image)

### 3.2: Ammonia Breakthrough Studies in Metallated UIO-66

The following procedure was followed for ammonia adsorption studies:
- Ammonia adsorption under dynamic conditions.
- Samples were activated in situ prior to the experiments.
- Breakthrough time= time needed for [NH₃]=50 ppm (OSHA PEL).
- Once the NH₃ effluent concentration reaches 500 ppm, the system is switched to a N₂ stream to start the desorption step.
- Repeatability of experiments: ±12%.

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<td>Adsorbent Volume</td>
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<td>Flow Rate</td>
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Breakthrough curves are shown in Figures 5 and 6 below.

**Figure 5:** Breakthrough curves for ammonia in UiO-66 at 298 K from dry air.

**Figure 6:** Breakthrough curves for ammonia in UiO-66 at 298 K from air with 80% RH.
Dynamic capacities calculated from the breakthrough curves for both metallated samples compared to the parent sample are given in Table 2. Several points can be inferred from the breakthrough curves and capacity results:

• NH₃ capacities increase by 36% and 125% for UiO-66-COOCu and UiO-66-(COOCu)₂, respectively.
• Binding energy of NH₃ is higher with –COOCu than with –COOH groups.
• Less steep slopes are an indication of mass transfer limitations.
• No unusual shapes infer that the materials are not decomposing after NH₃ exposure.
• No direct correlation between copper content and NH₃ loading.
• Breakthrough curves indicate mass transfer limitations.
• Materials are not decomposing after NH₃ exposure.
• No direct correlation between copper content and NH₃ loading.
• No capacity drop was observed for metal loaded MOFs.

Table 2: Dynamic Capacities for Each MOF under Dry and Wet (80% RH) Conditions.

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<td>¹⁵UiO-66-(COOH)₂</td>
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In conclusion, we have found that metal-inserted UiO-66-(COOH)₂ performs extremely well for ammonia removal and exhibits dynamic capacities above the target loading of 6 mmol g⁻¹. This point is significant: the metallated UiO-66 essentially provides performance that mimics open metal site MOFs, while also maintaining the excellent stability and robustness expected for UiO-66.

To give further insight into the state of the copper, we have also synthesized UiO-66, unfunctionalized, and performed a wet impregnation of copper nitrate. In this case, the copper nitrate should not be bound to anything and will remain intact either on the surface of the crystals or inside the pore space. Ammonia breakthrough tests show that these impregnated samples perform almost identically to UiO-66 without copper nitrate impregnation. This result is in stark contrast to the ammonia adsorption results in the metal-inserted samples. This provides further evidence, albeit indirectly, that the metal-inserted samples truly possess copper carboxylate groups.

REFERENCES:


**Keynote Addresses and Plenary Lectures**


Invited Conference and Workshop Presentations


16. Surface Science Colloquium, Edgewood Chemical Biological Center, Edgewood, MD, December 9, 2009.


