

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) 15-10-2018		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Oct-2015 - 30-Sep-2016	
4. TITLE AND SUBTITLE Final Report: Advanced Processing of Multifunctional Materials for Adsorptive Removal and Sensing of Chemical Warfare Agents			5a. CONTRACT NUMBER W911NF-15-1-0640		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Georgia Tech Research Corporation 505 Tenth Street NW Atlanta, GA 30332 -0420			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 67991-CH.4		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Krista Walton
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 404-385-7499

RPPR Final Report
as of 09-Nov-2018

Agency Code:

Proposal Number: 67991CH

Agreement Number: W911NF-15-1-0640

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EIN: 580603146

Report Date: 31-Dec-2016

Date Received: 15-Oct-2018

Final Report for Period Beginning 01-Oct-2015 and Ending 30-Sep-2016

Title: Advanced Processing of Multifunctional Materials for Adsorptive Removal and Sensing of Chemical Warfare Agents

Begin Performance Period: 01-Oct-2015

End Performance Period: 30-Sep-2016

Report Term: 0-Other

Submitted By: Krista Walton

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1

STEM Participants:

Major Goals: See attachment

Accomplishments: See attachment

Training Opportunities: Nothing to Report

Results Dissemination: Publication resulted in 2016

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Krista Walton

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: William Mounfield III

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

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as of 09-Nov-2018

National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: William Mounfield III

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

ARTICLES:

Publication Type: Journal Article

Peer Reviewed: Y

Publication Status: 1-Published

Journal: Industrial & Engineering Chemistry Research

Publication Identifier Type: DOI

Publication Identifier: 10.1021/acs.iecr.6b01045

Volume: 55

Issue: 22

First Page #: 6492

Date Submitted:

Date Published: 5/1/16 4:00AM

Publication Location:

Article Title: Synergistic Effect of Mixed Oxide on the Adsorption of Ammonia with Metal–Organic Frameworks

Authors: William P. Mounfield, Micaela Taborga Claire, Pradeep K. Agrawal, Christopher W. Jones, Krista S. Waz

Keywords: ammonia adsorption

Abstract: A hydrotalcite-derived MgAl oxide (MMO) was evaluated in combination with the metal-organic frameworks (MOFs) UiO-66 and UiO-66- NH₂ for the adsorption of ammonia. Analysis of the materials' textural properties after ammonia breakthrough adsorption revealed no change in the PXRD patterns or FTIR spectra; however, a slight decrease in surface area was observed, consistent with the hypothesized presence of strongly adsorbed species after adsorption. UiO-66:MMO and UiO-66-NH₂:MMO composites maintained ammonia adsorption capacity under dry conditions. An almost 2-fold increase in humid ammonia capacity was observed for the UiO-66:MMO composite, far beyond that expected through a linear combination of the two materials' capacities. The synergistic effect observed in humid conditions was further investigated with water adsorption experiments, which suggested the effect is the result of the high water affinity of MMO.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

DISSERTATIONS:

Publication Type: Thesis or Dissertation

Institution: Georgia Institute of Technology

Date Received: 15-Oct-2018

Completion Date: 12/6/16 4:45PM

Title: Acid and Base Gas Exposure and Solvent Effects on Metal-Organic Framework Structure and Gas Adsorption Properties

Authors: William Mounfield

Acknowledged Federal Support: Y

RPPR Final Report
as of 09-Nov-2018

ADVANCED PROCESSING OF MULTIFUNCTIONAL MATERIALS FOR ADSORPTIVE REMOVAL AND SENSING OF CHEMICAL WARFARE AGENTS

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1.0 OVERVIEW, BACKGROUND, AND OBJECTIVES

1.1 OVERVIEW

The ability to manipulate and control matter at the nanoscale offers the potential for radical advances in how we produce chemicals, materials, and energy. The design of nanoscale structures provides access to physicochemical properties that are distinctly different and unattainable compared to the bulk phase. This control at the nanoscale is critical for advancing a broad spectrum of technologies ranging from adsorption separations, sensing, and catalysis to solar cells and lithium-ion batteries. The goal of this proposed research project is to develop advanced multifunctional materials and processing techniques that can be used for the removal, detection, or destruction of chemical warfare agents (CWAs). The proposed work will build on our previous research on metal-organic frameworks for removal of ammonia, carbon monoxide, and other toxic chemicals. A particular emphasis will be placed on creating engineered forms and composites of multifunctional nanopowders that are suitable for use in low-pressure drop CWA removal devices or for incorporation into chemical sensing arrays.

1.3 OBJECTIVES

The goal of this work was to develop tools and processing techniques for the fabrication of MOF composites. The flexibility afforded by these synthesis techniques will lead to potential advances in materials for CWA removal, sensing, and destruction.

2.0 DELIVERABLES

2.1 MAJOR DELIVERABLES FOR YEAR 1

- a) 3-6 new composites to be tested for adsorption of ammonia
- b) Formation and characterization of 2-4 pelletized MOFs with different formulations of MMO or zirconium hydroxide binder and refinement of methods.
- c) Testing of pelletized MOFs (minimum of 2-4 samples) for DMNP affinity and refine methods.

These deliverables resulted in a publication in I&EC Research: Mounfield et al., Synergistic Effect of Mixed Oxide on the Adsorption of Ammonia with Metal-Organic Frameworks, *Industrial & Engineering Chemistry Research*, 2016, 55, 6492—6600.

From the abstract: “A hydrotalcite-derived MgAl oxide (MMO) was evaluated in combination with the metal–organic frameworks (MOFs) UiO-66 and UiO-66-NH₂ for the adsorption of ammonia. Analysis of the materials’ textural properties after ammonia breakthrough adsorption revealed no change in the PXRD patterns or FTIR spectra; however, a slight decrease in surface area was

observed, consistent with the hypothesized presence of strongly adsorbed species after adsorption. UiO-66:MMO and UiO-66-NH₂:MMO composites maintained ammonia adsorption capacity under dry conditions. An almost 2-fold increase in humid ammonia capacity was observed for the UiO-66:MMO composite, far beyond that expected through a linear combination of the two materials’ capacities. The synergistic effect observed in humid conditions was further investigated with water adsorption experiments, which suggested the effect is the result of the high water affinity of MMO.”

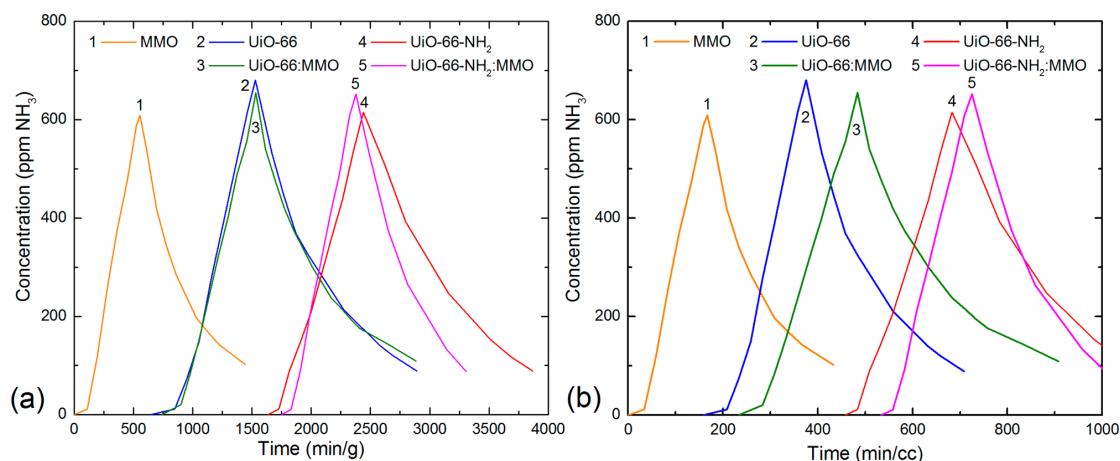
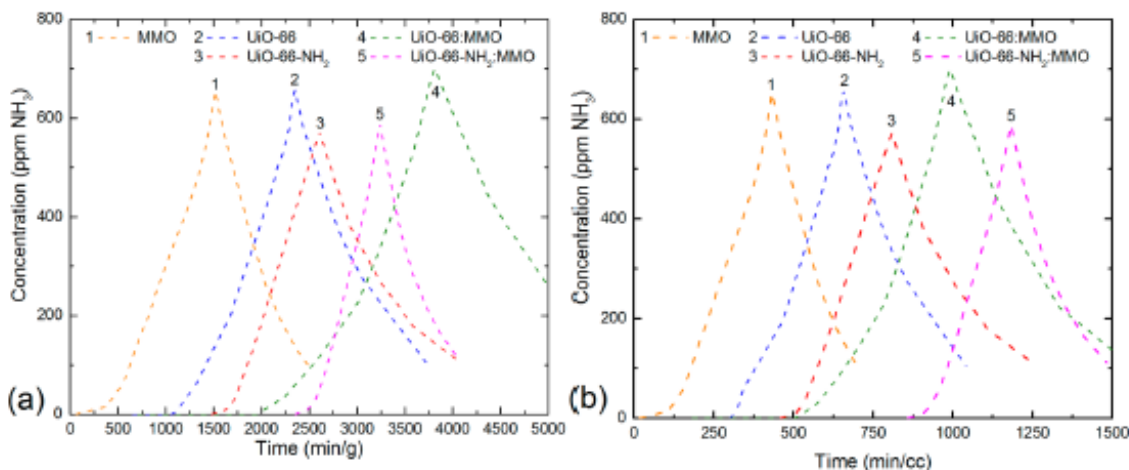


Figure 2 from the publication: Breakthrough and desorption curves for MMO, UiO-66, UiO-66-NH₂, UiO-66:MMO, and UiO-66-NH₂:MMO under dry conditions. Time is normalized either by (a) gram of total adsorbent mass in g or (b) total bed volume in cm³.



Taken from Figure 3: Breakthrough and desorption curves for MMO, UiO-66, UiO-66-NH₂, UiO-66:MMO, and UiO-66-NH₂:MMO under wet conditions. Time is normalized either by (a) gram of total adsorbent mass in g or (b) total bed volume in cm³.

Table 2. Calculated Dynamic Ammonia Capacity for All Materials and Composites^a

material	dry NH ₃ exposure capacity (mmol/g)	wet NH ₃ exposure capacity (mmol/g)
UiO-66	1.84	2.63
UiO-66-NH ₂	3.25	3.18
MMO	0.68	1.50
HT	0.66	1.25
UiO-66:MMO	1.89 (2.26)	5.06 (6.07)
UiO-66:HT	1.51 (1.81)	2.00 (2.40)
UiO-66-NH ₂ :MMO	3.48 (4.18)	4.06 (4.87)

^aBreakthrough capacity is calculated by extrapolation and integration to 1500/1483 ppm, respectively. Values shown in parentheses are normalized per gram of MOF.

Several major conclusions resulted from this work:

- Addition of MMO to UiO-66 in a 5:1 MOF:MMO ratio resulted in almost a 2-fold increase in wet ammonia adsorption performance above the pure MOF capacity, although the MMO alone possesses poor performance.
- The effect in humid conditions is hypothesized to be 2-fold, benefiting from a water withdrawing effect allowing adsorption sites to remain open for ammonia adsorption and the solubility of ammonia in the water adsorbed on the MMO.
- In dry conditions, the addition of MMO did not negatively affect adsorption performance, usually the case with the addition of a poorly adsorbing binding material.
- These composites showed promise as multiuse adsorbents, as the initial breakthrough capacity and synergistic effect was preserved through three consecutive exposures for the UiO-66:MMO composite in wet conditions.